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Control of Air Pollution Emissions from Molybdenum Roasting. Volume 2. Alternatives for Control of Weak Sulfur Dioxide Emissions

Molycorp, Inc., Washington, PA

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- Limestone FGD
- Dual Alkali
- Magnesium Oxide
- Wellman-Lord
- Sulf-X
- Endako
- Chiyoda Thoroughbred 121
- U.S. Bureau of Mines Citrate
- Sodium Carbonate Throwaway
- Dowa Basic Aluminum Sulfate
- CIBA-GEIGY Nitrosyl-Sulfuric Acid Process
- CIBA-GEIGY SO_2 Sorption-Steam Stripping Process

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CONTROL OF AIR POLLUTION EMISSIONS FROM MOLYBDENUM ROASTING
VOLUME II
ALTERNATIVES FOR CONTROL OF WEAK SULFUR DIOXIDE EMISSIONS

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This document is one of a series of three reports resulting from a program to define the emissions control problems and explore applicable systems to control emissions from a molybdenum roaster. The program was jointly sponsored by Molycorp, Inc. and the Industrial Environmental Research Laboratory - Cincinnati to: (1) determine the capabilities of a unique fabric filtration system using teflon coated bags in a hot, corrosive atmosphere for particulate and trace element control and (2) to explore the feasibility of a variety of weak SO_2 control systems for application to the moly roaster and potentially to other smelter weak SO_2 off-gases.

David G. Stephen
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CIBA-GEIGY Nitrosyl-Sulfuric Acid Process
CIBA-GEIGY SO_2 Sorption-Steam Stripping Process
Limestone FGD
Dual Alkali
Magnesium Oxide
Wellman-Lord
Sulf-X
Endako
Chiyoda Thoroughbred 121
U.S. Bureau of Mines Citrate
Sodium Carbonate Throwaway
Dowa Basic Aluminim Sulfate

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SECTION 1

INTRODUCTION

Radian Corporation, in support of a program co-sponsored by Molycorp, Inc. and the U.S. Environmental Protection Agency, has conducted a program examining particulate and sulfur dioxide abatement measures for nonferrous smelters. The three principal phases of this program were: (1) characterization of particulate control of a molybdenum sulfide roaster by fabric filtration, (2) assessment of sulfur dioxide abatement alternatives, and (3) pilot testing of the magnesia slurry process for sulfur dioxide control. The assessment of sulfur dioxide abatement alternatives is the focus of this report. The first two phases of the program are discussed in companion publications from the Environmental Protection Agency.

Molycorp operates two multilevel hearth roasters processing ten million pounds of molybdenum per year at their Washington, Pennsylvania facility. In the roasting process molybdenum disulfide concentrate is oxidized by air to molybdenum trioxide and sulfur dioxide. Experiments were performed with a bench-scale lime based SO_2 wet scrubber at the Molycorp facility to generate waste solids for characterization and to evaluate scrubber performance. Several different flue gas desulfurization (FGD) technologies which were developed for use in the electric utility industry were then evaluated for use on nonferrous smelters. Using the Molycorp roaster offgas as the design basis, a conceptual design was prepared for a limestone FGD system and system costs were determined.

Since the abatement of sulfur dioxide emissions from nonferrous smelters is an advancing technology area, an assessment of two developing technologies was also performed. This assessment included visits to the process developer's facilities in Western Europe to obtain the most recent information. The two processes are flue gas cleaning system developed by Ciba-Geigy.

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SECTION 2

TWO DEVELOPING TECHNOLOGIES FOR ABATEMENT OF SULFUR DIOXIDE EMISSIONS

This section documents the status of two sulfur dioxide abatement technologies being developed in Western Europe. The technologies discussed are: (1) the Ciba-Geigy Nitrogen Oxide-Sulfuric Acid Process and (2) the Ciba-Geigy SO_2 Sorption-Steam Stripping Processes. The two Ciba-Geigy processes are pollution control technologies that are applicable to a variety of gaseous emission streams from nonferrous smelters.

2.1 THE CIBA-GEIGY NITROGEN OXIDE-SULFURIC ACID PROCESS

2.1.1 Introduction

SO_2 removal from gases containing 1-2 percent SO_2 poses problems for most conventional sulfur dioxide control processes. Streams with an SO_2 content in this concentration range occur frequently, especially in the nonferrous metals industry. This problem was solved with the application of the Ciba-Geigy nitrosyl-sulfuric acid process for molybdenum roaster offgases at a facility operated by H. C. Starck, Berlin, at their Goslar plant (Figure 1).

Several SO_2 control processes offered in West Germany were considered by H. C. Starck personnel. Among them were those processes offered by Babcock, Bischoff, Steinmuller and Lurgi. It was found that these processes were developed for different conditions of temperature, SO_2 concentration and gas flow rate than those in molybdenum roaster offgases.

Theoretical evaluations were verified in pilot-scale tests. The sulfazid process removed only 18 percent of the SO_2 and produced a 10 percent H_2SO_4 stream. Lime scrubbing achieved 60 percent SO_2 removal and produced a sulfite sludge which caused disposal problems. The catalytic oxidation process proved uneconomic for flue gases of low SO_2 and high H_2O content.

The process of choice was finally the nitrosyl-sulfuric acid process which was optimized by Dr. V. Fattinger, Ciba-Geigy, Basel, Switzerland. This process was attractive because it is able to handle flue gas with SO_2 concentrations in the 0.5-2 percent range. Advances in material development (plastics) solved corrosion problems plaguing sulfuric acid production via the lead chamber route. The process is controlled through simple measurements

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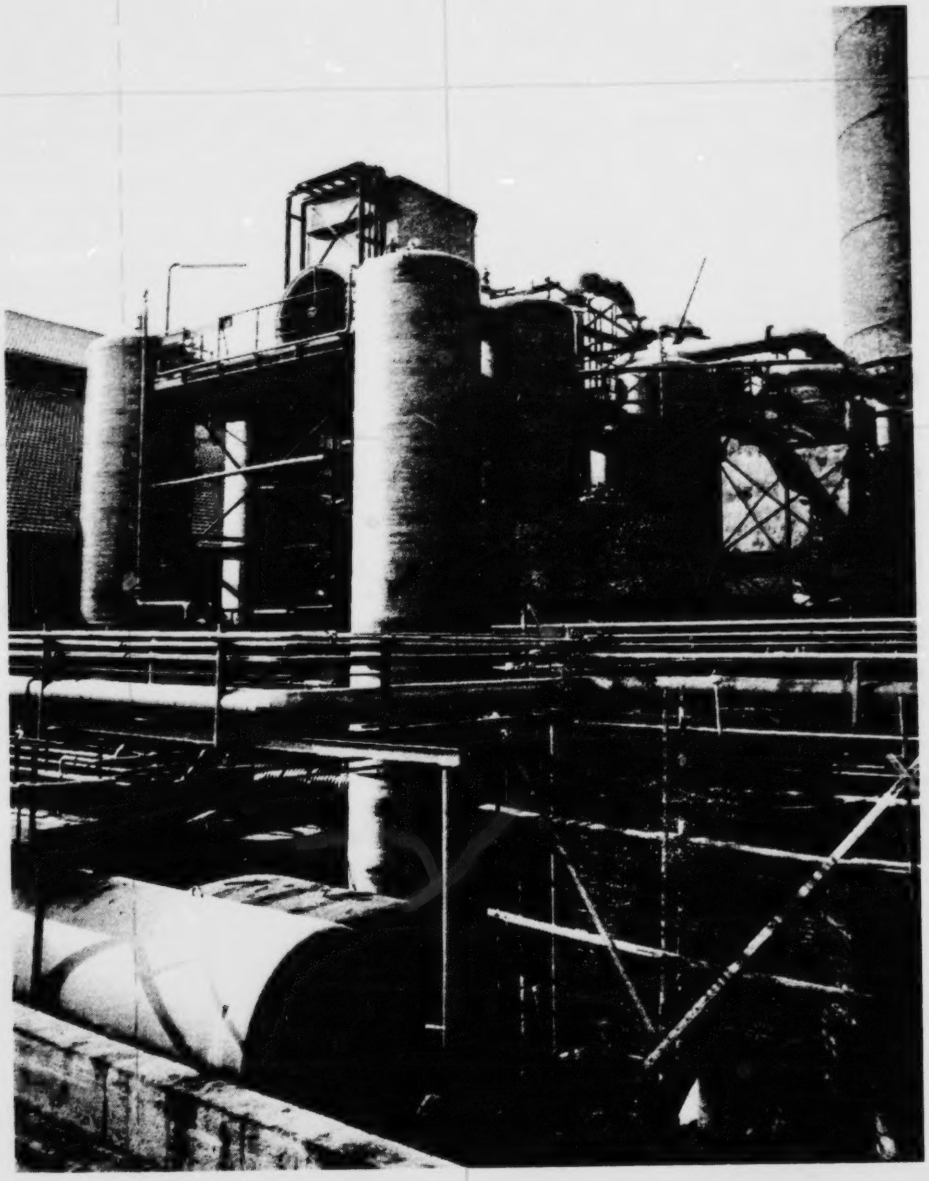

Figure 1. Installation in Goslar (height of towers 12m, diameter of towers 2.7m)

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like pressure, level height, density and temperature. These improvements made full automation feasible. Finally, the 75 percent H_2SO_4 produced in the nitrosyl-sulfuric acid scheme was found to be useful in a by-product recovery application.

The Ciba-Geigy nitrosyl-sulfuric acid process is based on the classic lead chamber process. The chemistry of this process is reviewed in the next section. A description of the application of the chemistry in a modern production plant follows. Then the process controls are discussed. A description of the Goslar plant follows. Cost information is given last.

This report is based on oral information received during a visit at Basel (1). Other documents used were the papers by:

1) Dr. V. Fattinger, Ciba-Geigh Ltd. Basel (2).

2) Klaus Blankenstein, G. E. Neumann, Firma H. C. Starck, Berlin (3).

2.1.2 Process Chemistry

The Ciba-Geigy process for the control of SO_2 and NO_x was developed from the classic lead chamber process shown in Figure 2. The discussion of the underlying chemical reactions is based on this process. Sulfuric acid is formed through catalytic oxidation of sulfur dioxide with nitrogen oxide acting as a catalyst. The SO_2-air mixture enters the Glover tower, passes to the lead chambers and exits through the Gay Lussac tower. (The gas flow is not shown in Figure 2). The fluid-gas contact in the packed towers is countercurrent.

The major part of the sulfuric acid is formed in the lead chambers according to the following equations:

$$\begin{array}{r} NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad\qquad \\ NO_2 + SO_2 \rightarrow SO_3 + NO \\ \underline{SO_3 + H_2O \rightarrow H_2SO_4 \qquad} \\ \tfrac{1}{2}O_2 + SO_2 + H_2O \rightarrow H_2SO_4 \qquad\qquad \end{array} \qquad (1)$$

The nitrogen oxides are generated through decomposition of nitrosyl-sulfuric acid and nitric acid in the Glover tower (denitration tower) and are reabsorbed in sulfuric acid in the Gay-Lussac towers (nitrogen oxide absorption towers). Nitrosyl-sulfuric acid is the mixed anhydride of sulfuric acid and nitrous acid or of sulfurous acid and nitric acid. It is stable only in a strongly hygroscopic environment such as concentrated sulfuric acid.

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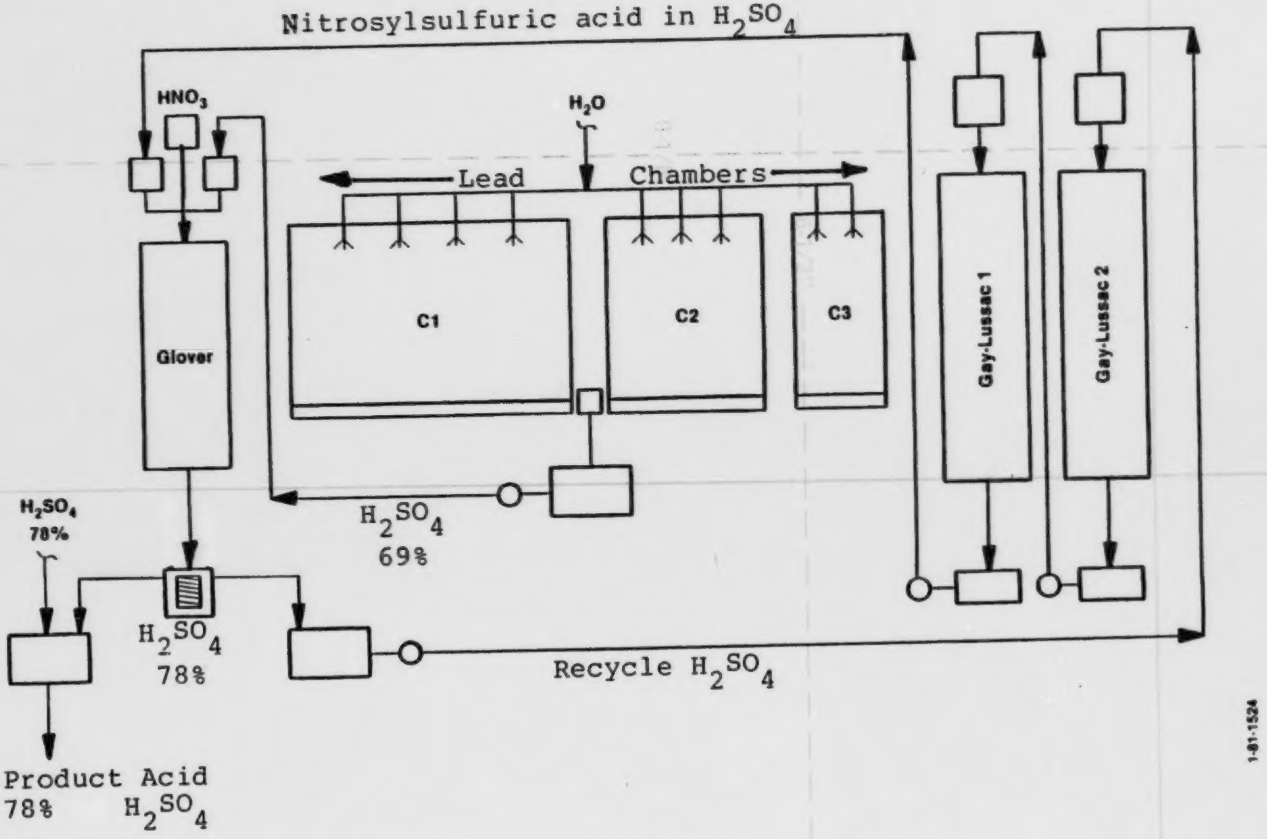
Nitrosylsulfuric acid in H_2SO_4
HNO_3
H_2O
Lead Chambers
Glover
C1
C2
C3
Gay-Lussac 1
Gay-Lussac 2
H_2SO_4 69%
H_2SO_4 78%
H_2SO_4 78%
Recycle H_2SO_4
Product Acid 78% H_2SO_4
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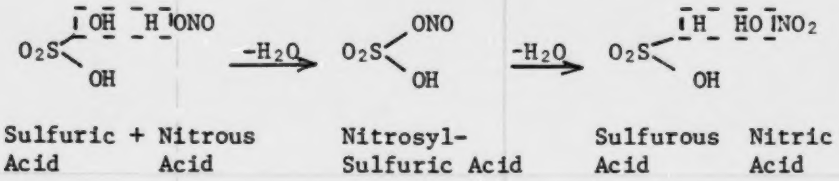
Figure 2. Schematic of the lead chamber process.



(2)

It decomposes readily in contact with water:

$$HSO_4{\cdot}NO + H_2O \rightarrow H_2SO_4 + HNO_2 \qquad (3)$$

The reactions in the Glover tower (78% H_2SO_4) are NO formation from nitrosylsulfuric acid:

$$2HSO_4{\cdot}NO + 2H_2O + SO_2 \rightarrow 3H_2SO_4 + 2NO \qquad (4)$$

and decomposition of nitric acid:

$$2HNO_3 + 3SO_2 + 2H_2O \rightarrow 3H_2SO_4 + 2NO \qquad (5)$$

The liberated NO is carried together with oxygen and SO_2 to the lead chambers where reaction 1 occurs. The NO containing gases free of SO_2 are treated for NO_x recovery in the Gay Lussac towers:

$$O_2 + 2NO + H_2SO_4 \rightarrow HSO_4{\cdot}NO + HNO_3 \qquad (6)$$

The effluent from the Gay Lussac towers is recirculated to the Glover tower.

The lead chamber process shown in Figure 2 consists of one acid cycle. Acid formed in the lead chambers is removed as process acid at the same rate as it is formed. Nitrogen oxide losses with the offgases are replenished through nitric acid addition to the Glover tower. Process temperatures are about 80°C in the acid circuit and 55-70°C in the lead chambers. The cooling is caused by the water spray. The chamber acid (69%) is pumped to the Glover tower and concentrated to 78 percent.

2.1.3 Process Description

Several changes to the lead chamber process have been developed to increase reaction rates. H. Peterson replaced the open lead chambers with packed production towers. Scientists at Ciba-Geigy observed that the SO_2 oxidation rate is increased if the sulfuric acid concentration of the chamber acid is between 59 and 66 percent and if traces of nitric acid are added. The denitration step is favored by high temperatures and high acid concentration, while nitrous oxide absorption is more complete at low temperatures.

V. Fattinger at Ciba-Geigy, Basel, optimized these findings in his nitrosyl-sulfuric acid process. A process schematic is shown in Figure 3. The process consists of three separate sulfuric acid cycles, namely:

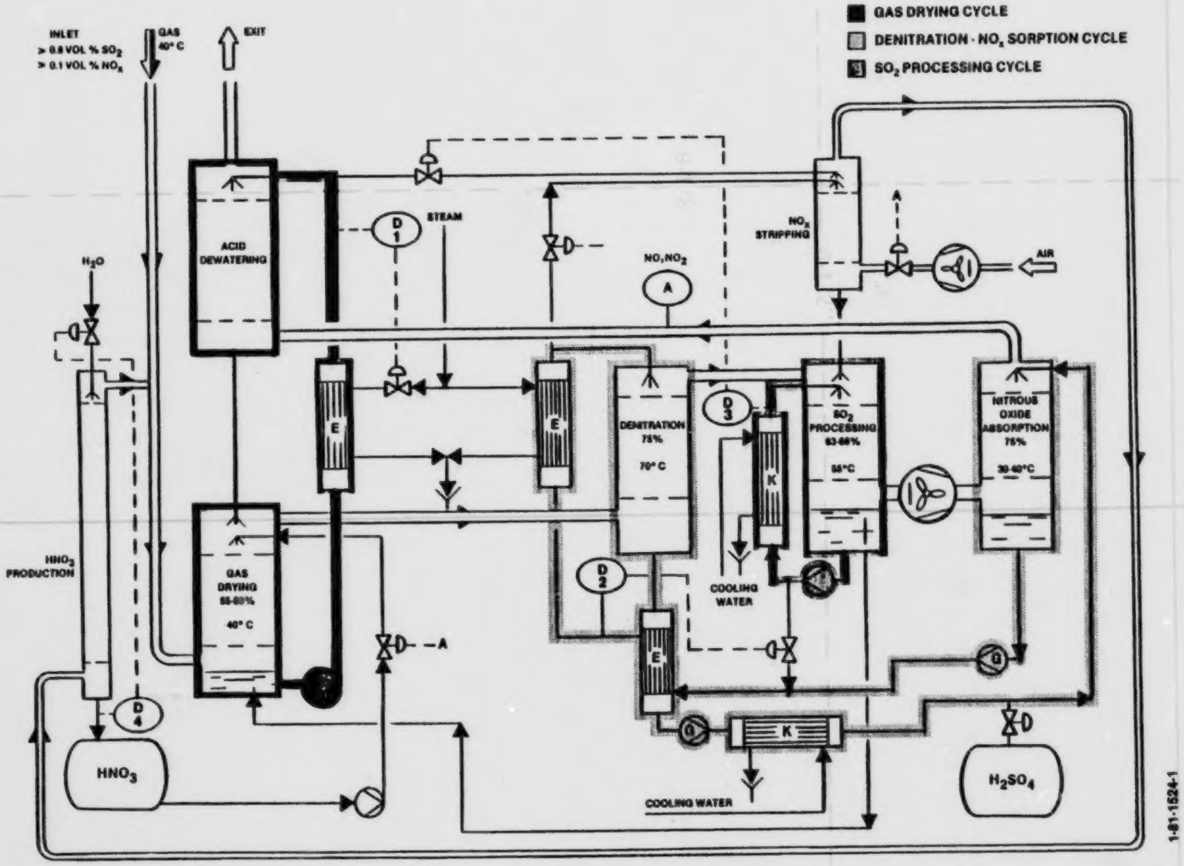

INLET
> 0.8 VOL % SO₂
> 0.1 VOL % NOₓ
GAS
40° C
EXIT
GAS DRYING CYCLE
DENITRATION · NOₓ SORPTION CYCLE
SO₂ PROCESSING CYCLE
ACID DEWATERING
D 1
STEAM
H₂O
E
E
NO,NO₂
A
NOₓ STRIPPING
A
AIR
HNO₃ PRODUCTION
GAS DRYING 55-60% 40° C
A
DENITRATION 75% 70° C
D 3
K
SO₂ PROCESSING 63-66% 55°C
NITROUS OXIDE ABSORPTION 75% 30-40°C
D 2
COOLING WATER
E
D 4
HNO₃
K
COOLING WATER
H₂SO₄
1-81-1524-1

Figure 3. Process flow diagram of the Ciba-Geigy NO_x-H_2SO_4 process.

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- the gas drying cycle,
- the denitration - NO_x sorption cycle, and
- the SO_2 processing cycle.

The purpose of the gas drying cycle is to achieve the H_2O:SO_2 ratio necessary for the production of 75 percent H_2SO_4. Incoming gases are contacted with sulfuric acid of a preselected concentration and temperature. Normally, an acid concentration between 55 and 60 percent is chosen. Given the concentration, the water vapor pressure can be adjusted by choosing the right temperature. For example, the water vapor pressure changes by two orders of magnitude if the temperature of a 60 percent acid is raised from 25°C to 100°C (see Figure 4).

The water vapor removed from the gas in the drying tower is expelled in the following acid dewatering tower, where the H_2O-rich sulfuric acid is contacted with the very dry process offgases. Increase of the temperature by a heat exchanger increases the driving force for H_2O release. The dewatered sulfuric acid then again contacts the incoming wet raw gases.

The second cycle is the denitration - NO_x absorption cycle. Decomposition of nitric acid and nitrosyl-sulfuric acid is achieved in a packed tower at 70°C. The stripped acid from this tower is cooled to 30-40°C and contacted in a packed absorption tower with the SO_2-free, H_2O-free, but NO_x-laden gases coming from the processing cycle.

The third cycle is the SO_2 processing cycle. The acid concentration is 63-66 percent and the temperature is 55°C. The majority of the SO_2 oxidation takes place in the SO_2 processing tower. However, some sulfuric acid is also formed in the gas drying and denitration towers. This necessitates removal of acid in a slipstream in order to avoid a steady increase in the acid concentration. The 55-60 percent acid from the gas drying cycle is fed to the 63-66 percent acid in the processing cycle, and the acid produced in the processing cycle is fed to the 75 percent acid in the denitration-NO_x sorption cycle. Product acid is removed from the bottom of the denitration tower.

The nitrosyl-sulfuric acid process can be used for nitric acid production if the NO_x concentration of the incoming gases is high enough. Nitrogen compounds build up in the sulfuric acids of the drying and denitration-NO_x absorption cycles. The excess nitrogen oxides are removed in a NO_x stripper and contacted with water in the HNO_3 production column. Both the stripping column and the HNO_3 production column are shown in Figure 3. In cases where gases of low NO_x concentration are treated for SO_2 removal, nitric acid is fed to the process to supply the NO_x catalyst. The NO_x concentration of the exit gases is ultimately a function of the absorption tower size. Low NO_x concentration in the exit gas requires large absorption towers, which means high costs. Concentrations of 100-250 ppm NO_x are achievable if the absorption towers are designed properly.

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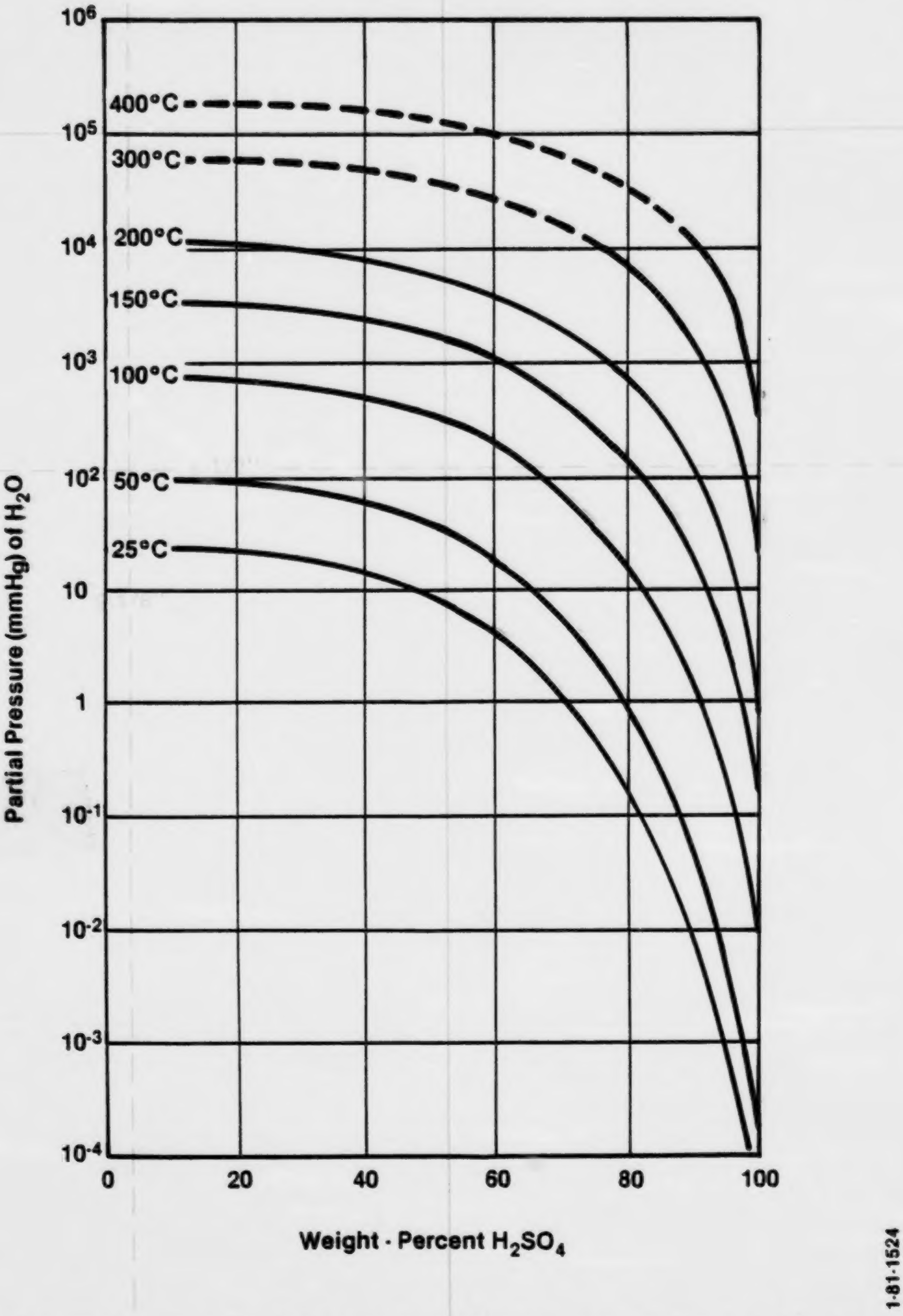

Figure 4. The partial pressure of water over aqueous sulfuric acid. Reproduced with permission of Ciba-Geigy

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The 75 percent sulfuric acid can be concentrated to 98 percent. Preconcentration through H_2O evaporation produces 88 percent H_2SO_4. A small catalytic unit can be used to produce a concentrated acid of 98 percent. A suitable scheme is shown in Figure 5.

2.1.4 Process Control

Process control is based on the measurement of the following parameters:

- Temperature
- Gas pressure
- Filling height
- Density of sulfuric acid
- NO, NO_2 concentration in outlet gas
- SO_2 concentration

The simplicity of these controls allows the process to be fully automated.

The sulfuric acid concentration in the three cycles is controlled through density and temperature. The H_2SO_4 concentration in the gas drying cycle is measured at the point D-1 marked in Figure 3. Point D-1 is located at the inlet to the acid dewatering tower. The degree of acid dewatering is a function of the water vapor pressure of the acid, which is a function of temperature. The temperature is controlled through the steam input to the heat exchanger E. Other possibilities are addition of SO_2 processing acid to the gas drying tower (increase in acid concentration) or acid bleed-off to the NO_x stripping tower (decrease in acid concentration).

The denitration cycle operates at a sulfuric acid concentration of 75 percent. The density control point is at D-2. An increase in acid concentration is counteracted by dilution with 65 percent acid from the SO_2 processing cycle. A bleed stream is taken from the denitration cycle and fed to the H_2SO_4 production tank.

The concentration of the SO_2 processing cycle is monitored at the tower inlet (D-3). An increase in H_2SO_4 concentration is counteracted through dilution with 60 percent acid from the gas drying cycle.

The nitrogen balance in the system is regulated by setting the NO and NO_2 concentration in the exit gas stream. This relative simple measurement is the most complicated one in the whole system. Nitric acid is added to the gas drying tower if the NO_x exit concentration deviates from the set point. The plant operates in this case in the HNO_3 consumption mode.

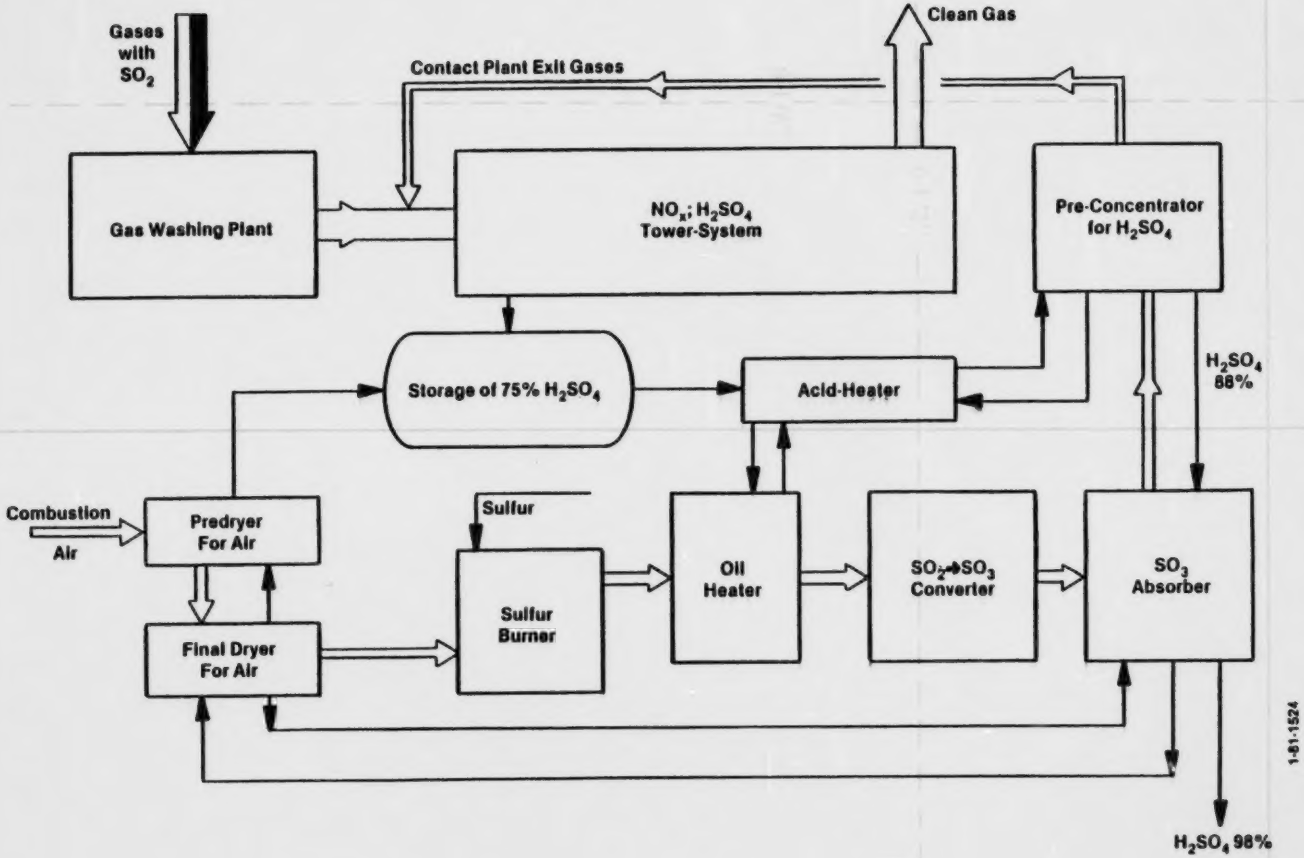
Gases with SO_2
Contact Plant Exit Gases
Clean Gas
Gas Washing Plant
NO_x; H_2SO_4 Tower-System
Pre-Concentrator for H_2SO_4
Storage of 75% H_2SO_4
Acid-Heater
H_2SO_4 88%
Combustion Air
Predryer For Air
Final Dryer For Air
Sulfur
Sulfur Burner
Oil Heater
$SO_2 \rightarrow SO_3$ Converter
SO_3 Absorber
1-81-1524
H_2SO_4 98%

Figure 5. Production of 98 percent sulfuric acid.
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Nitrogen oxides are stripped from the denitration NO_x-sorption cycle if the exit concentration of the nitrogen oxide is found to be above the set point. Stripping is done with air. The NO_x laden air exiting the stripping column is fed to the HNO_3 production column. The water addition rate to this column is regulated through HNO_3 density measurement at the column exit. The plant produces nitric acid in this operating mode.

The NO_x set point necessary for steady-state operation can be influenced through tower design. Generally, a low set point requires more theoretical stages in the sorption columns, which increases the costs of the operation.

Start-up and shutdown of the plant is reported to be very easy. Process stream temperatures do not exceed 80°C at any point in the process.

2.1.5 The Full-Scale Plant at Goslar

The company H. C. Starck, Berlin, operates a molybdenum roaster in Goslar, West Germany. This roaster has a capacity of 4000 tons of ore per year with about 2,500 tons of SO_2 produced as a by-product. Molybdenum roasting requires excess air which causes high gas flow rates with low SO_2 concentration. The gas flow at Goslar is about 10,000 Nm^3/h and the SO_2 content fluctuates between 0.5 and 2 percent.

Dust in the roaster offgas is first removed in a dry electrostatic precipitator with a reported efficiency of 99.5 percent. Fine cleaning is performed in a wet scrubber. The SO_2 containing gases entering the sulfuric acid plant are, therefore, saturated with water vapor.

The Goslar plant consists of 6 towers with a height of 12m and a diameter of 2.5m. Tower number 1 is divided into two sections. The $SO_2{:}H_2O$ ratio is adjusted in the lower half. Sulfuric acid drying is achieved in the upper part. Nitric acid is added in the dehydration part to equalize the NO_x losses with the stack gases.

In the second tower, nitrosyl-sulfuric acid and HNO_3 from the NO_x absorption section are decomposed. Part of the SO_2 is oxidized and the gas phase is laden with nitrogen oxides. Catalytic SO_2 oxidation and SO_3 absorption to form sulfuric acid are completed in towers number 3 and 4. The dry gases, which are practically SO_2 free, are fed to the NO_x absorption towers number 5 and 6 for nitrogen oxide recovery.

The scheme is practically the same as that in Figure 3. The main differences are the use of two SO_2 processing towers, two NO_x absorption towers, and the addition of a NO_x stripping column to reduce traces of NO_x in the produced acid. The unit at Goslar runs in the HNO_3 consumption mode. The temperature in the system never exceeds 80°C.

The size and design of all six towers are identical. The hulls are fabricated of glass fiber reinforced resins, coated with an acid resistant liner on the inside. Special plastic packing material with high surface area and low resistance to gas flow is used. The heat exchangers are fabricated from lead. Lead shows a high enough corrosion resistance to sulfuric acid at the temperatures encountered.

The exit gas contains less than 100 mg/m^3 (<35 ppm) SO$_2$. This corresponds to a removal efficiency of greater than 99 percent. Nitrogen oxide concentrations generated through the operation are less than 1000 mg/m^3 or 750 ppm. This is within the permissible limit set in West Germany. The NO$_x$ emission could be lowered by increasing the theoretical stages in the NO$_x$ sorption section.

The NO$_x$ concentration of 750 ppm compare to about 500 ppm from a coal-fired power plant. The total gas flow is, however, much higher in power plants.

The acid produced is reported to be clean. It is used internally for salt production. The plant which is fully automated is monitored from a central control room.

2.1.6 Cost

The costs for sulfuric acid and nitric acid production were estimated. They are graphically represented in Figures 6 and 7. These calculations are based on a gas throughput of 30,000 Nm^3/hr (Goslar 10,000 Nm^3/hr). Other assumptions were:

Lifetime of plant:	20 years
Interest rate:	7.5%
Cost of electricity:	5¢/kWh
Operating time:	8250 hrs/yr
SO$_2$ concentration:	0.5 to 8%
NO$_x$ concentration:	0.05 to 2%

The production cost per ton of H$_2$SO$_4$ increases rapidly for flue gases with a SO$_2$ concentration below 0.5 volume %. The NO$_x$-H$_2$SO$_4$ process is only competitive in this range if ways are found to preconcentrate the SO$_2$. Such procedures were also developed at Ciba-Geigy.

The mid-1980 production costs at Goslar were $90/ton. Optimization of the unit will lower these costs to $75/ton. These figures indicate that a plant processing more than 10,000 Nm^3/h containing a higher SO$_2$ content will be competitive in the West German economy.

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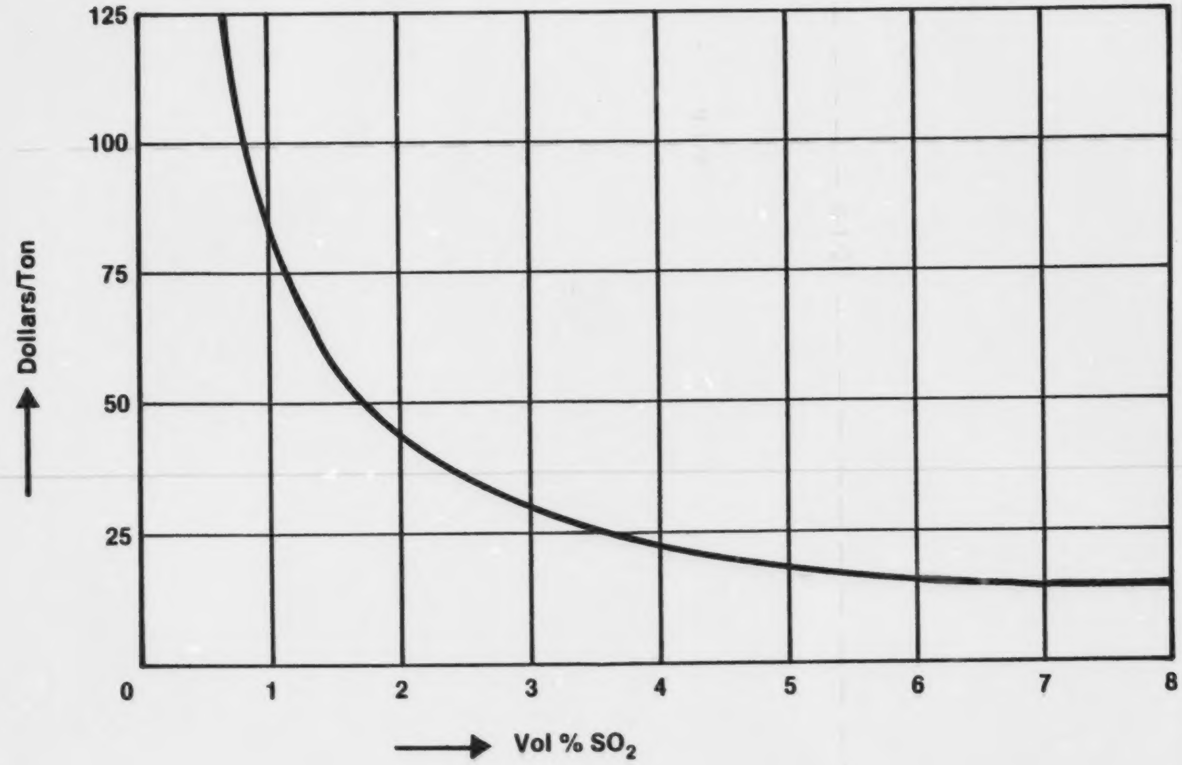

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Figure 6. 1980 Production cost per ton of sulfuric acid as function of the sulfur dioxide concentration in the flue gas.

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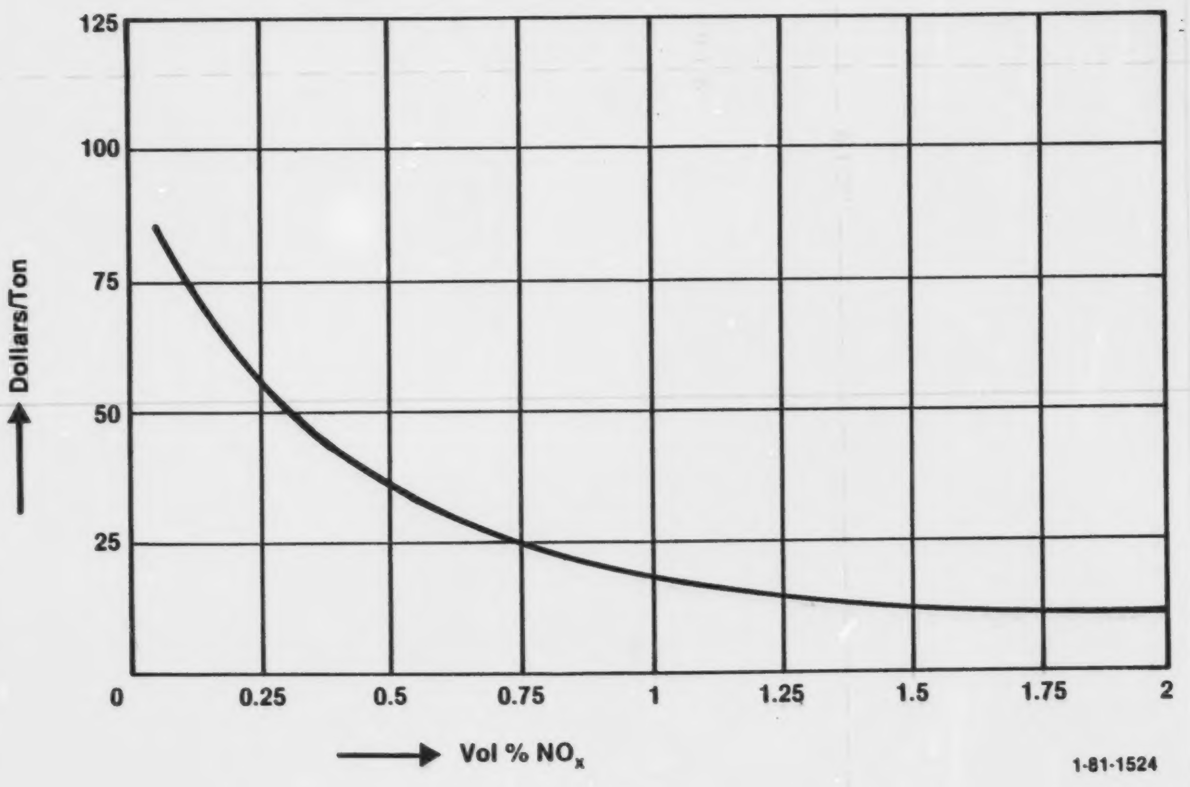

Figure 7. 1980 Production costs per ton of nitric acid as function of NO_x concentration in the flue gas.

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Estimates of HNO_3 production costs are shown in Figure 7. The basis is the same as that for the estimate in Figure 6. The production price per ton HNO_3 increases with decreasing NO_x content in the flue gas. This means that the amount of NO_x emissions are governed by cost considerations and not by technical feasibility.

German laws put the Goslar plant into the same category as incineration facilities. Maximum permissible NO_x concentrations are $1g/Nm^3$ or 750 ppm.

2.2 THE CIBA-GEIGY SO_2 SORPTION-STEAM STRIPPING PROCESS

2.2.1 Introduction

Ciba-Geigy developed an SO_2 sorption-steam stripping process based on aluminum sulfite as scrubbing solution. The purpose of this process is to enrich the sulfur dioxide concentration while treating streams containing low levels of SO_2.

There are several advantages to using aluminum sulfite-based scrubbing solutions. The vapor pressure of this inorganic compound is negligible; therefore, losses through evaporation (e.g., in the dimethylaniline enrichment approach) are avoided. In addition, the pH of the solution can be fine-buffered by adding elemental aluminum granules into the cycle; thus, sulfuric acid generated through SO_2 oxidation is neutralized.

The degree of SO_2 oxidation in this process has been found to be only 0.5 percent. This is partly due to the absence of oxidation catalysts which are removed in the gas cleaning section, and to maintaining process temperatures below 80°C. This upper temperature limit is set by the stability of the aluminum sulfite solution.

The small amount of sulfate formed is removed through precipitation as $CaSO_4 \cdot 2H_2O$. This operation is done by treating a slipstream. The precipitation operation adds little to the overall costs because part of the equipment used is needed anyway for sludge removal from the gas cleaning section.

The vapor pressure of SO_2 over aqueous aluminum sulfite shows a strong temperature dependence. This is advantageous since it lessens the necessary energy input into the desorption column.

The SO_2 removal efficiency depends on several variables. The sorption temperature has the greatest effect on SO_2 removal efficiency. The lower limit is actually dictated by the temperature of the available cooling water. The degree of SO_2 stripping in the desorption column also has great influence on removal efficiency. This can be increased by increasing the heat (steam) input. A third variable influencing SO_2 removal is the SO_2 concentration in the incoming flue gas. The removal efficiency increases with increasing SO_2 concentrations in the raw gas. Increasing the L/G ratio also can improve removal efficiency. Lowering the desorption pressure has only a minor effect. Normal operating pressures are in the 150-225 torr range.

Two process examples are given in this section. The first shows a high gas flow rate and a low SO_2 concentration, and the second, a low gas flow rate but a high SO_2 concentration. The effect on the energy input will be discussed.

This section is based on information released during a visit to Ciba-Geigy in October 1980. The author thanks Dr. Volker Fattinger and Dr. Walter Straumann for their cooperation.

2.2.2 Process Description

A schematic of the Ciba-Geigy sorption-steam stripping process is shown in Figure 8. It can be divided functionally into four sections:

- The gas cleaning cycle
- The SO_2 sorption-desorption cycle
- The blowdown cycle
- The SO_2 recovery cycle

Gas Cleaning Cycle--
The raw gas first enters the gas cleaning cycle. It consists of a conditioning tower and a closed pumping loop. The cleaning tower contains a bed of hedgehog packing, a venturi scrubber and a demister section. Fresh water is added to the demister section.

Particulate matter settled at the column bottoms and is discharged to the settling and neutralizer tank of the blowdown cycle.

SO_2 Sorption-Desorption--
The cleaned gas next enters the SO_2 absorption column. This, too, is a packed tower. The SO_2 is contacted countercurrently with a 19.5 g/ℓ aluminum sulfite solution. The temperature of the sorbing solution, determined by the temperature of the available cooling water, is in the 20-40°C range. The SO_2 removal efficiency increases with decreasing temperature of the scrubbing agent.

Cleaned gas is ducted to the stack. The effluent stream (bottom) from the SO_2 sorption column is heated to 70-80°C before entering the desorption tower. Heating is achieved in two steps. In step one, the cold SO_2 sorption column effluent is contacted in a countercurrent heat exchanger (not shown in Figure 8) with the hot SO_2 desorption column effluent. In step two, a further temperature increase is achieved in a heat exchanger fed with steam.

The brine has a temperature of 70-80°C at this point. It is fed next to the SO_2 desorption column, which is also a packed contactor. Water and SO_2 are stripped off the sorbent by applying a vacuum. Typical pressures in the column are between 150 and 225 torr. Lower pressures are uneconomical. The degree of the SO_2 desorption can be greatly influenced by the addition of steam.

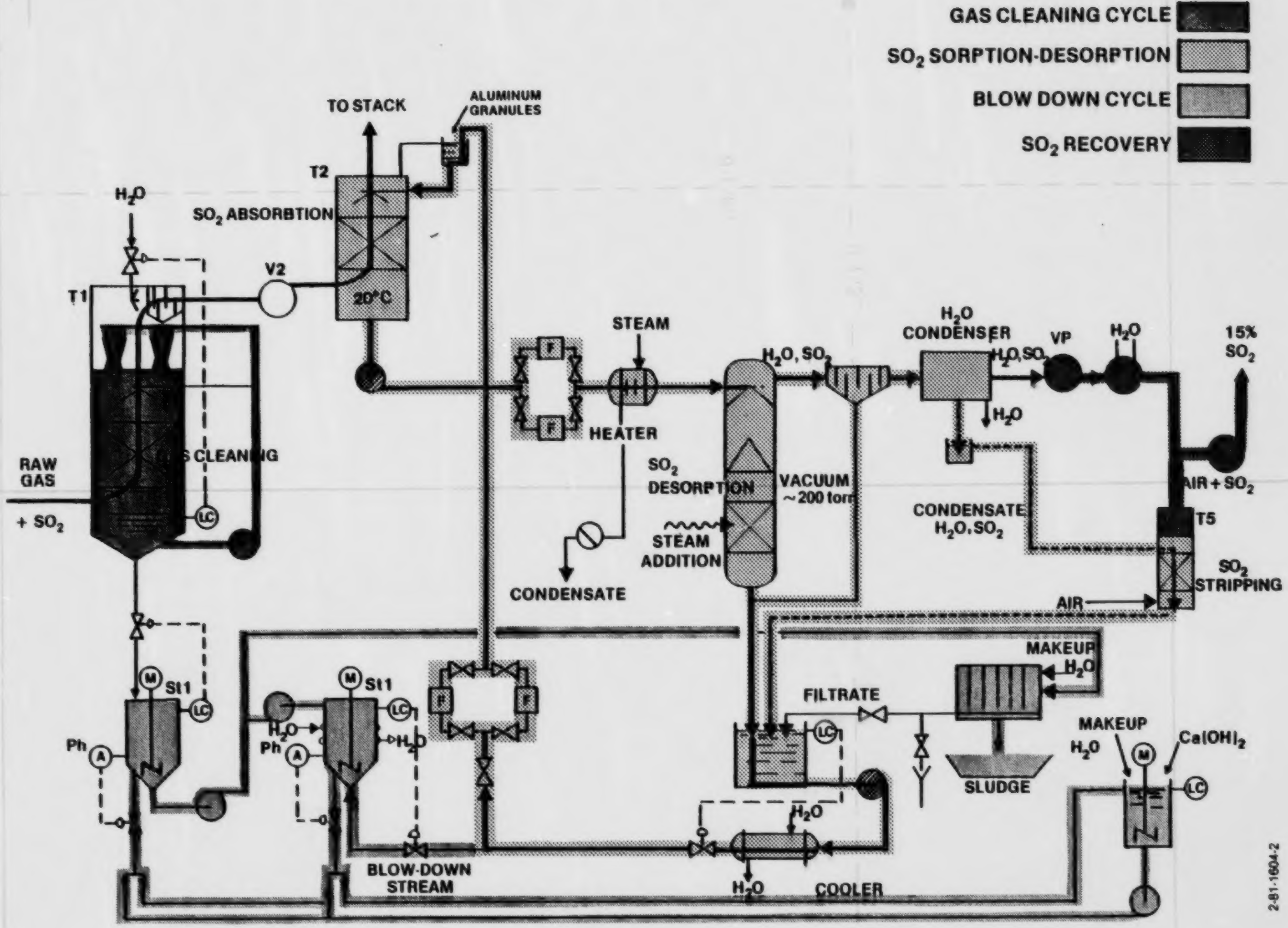
GAS CLEANING CYCLE
SO_2 SORPTION-DESORPTION
BLOW DOWN CYCLE
SO_2 RECOVERY
TO STACK
ALUMINUM GRANULES
T2
H_2O
SO_2 ABSORBTION
V2
T1
20°C
RAW GAS
+ SO_2
GAS CLEANING
LC
STEAM
HEATER
CONDENSATE
SO_2 DESORPTION
STEAM ADDITION
VACUUM ~200 torr
H_2O, SO_2
H_2O CONDENSER
H_2O, SO_2
H_2O
VP
H_2O
15% SO_2
AIR + SO_2
T5
CONDENSATE H_2O, SO_2
SO_2 STRIPPING
AIR
MAKEUP H_2O
FILTRATE
SLUDGE
MAKEUP H_2O
$Ca(OH)_2$
M
St1
Ph
A
BLOW-DOWN STREAM
COOLER
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Figure 8. Schematic of the Ciba-Geigy SO_2 sorption-steam stripping process. Reproduced with permission of Ciba-Geigy

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The desorption column effluent, stripped of SO_2, is cooled. This again is achieved in two steps. First, the effluent is contacted in the countercurrent heat exchanger (not shown in Figure 8) with the cold SO_2 sorption column effluent; next it is further cooled in a heat exchanger.

The sorbent then is finally contacted with elemental aluminum before entering the SO_2 sorption column. Elemental aluminum acts as a fine buffer by reacting with H_2SO_4 formed through oxidation of SO_2.

The overhead of the desorption column contains water droplets, water vapor and SO_2. First, it enters a demister and then a condenser. The demister effluent is combined directly with the SO_2 desorption column effluent in a hold tank. The condensate consists of an acidic, aqueous SO_2 solution. First, it enters an SO_2 stripping column, then it is combined with the main stream in a hold tank.

SO_2 Recovery--

Only the initial part of the SO_2 recovery is shown in Figure 8. The gas is removed from the condenser with a vacuum pump, further cooled, and combined with the overhead of the SO_2 stripping column, which removes the SO_2 from the condenser effluent.

The SO_2 concentration at this point is approximately 15 percent. Recovery of the SO_2 can be achieved by any processes developed for treatment of flue gases with high SO_2 concentration. Examples are the Ciba-Geigy nitrosylsulfuric acid process, SO_2 liquefaction, catalytic oxidation, etc.

Blowdown Cycle--

Two sources feed solid material to the blowdown cycle. The first source is the flue gas conditioning tower. The solids collected are fed in the form of a slurry to a settling and neutralizer tank. pH adjustment is achieved by adding a $Ca(OH)_2$ solution. The second source is the gypsum precipitation tank. Here a slipstream from the sorption-desorption cycle is treated for sulfate removal. Gypsum is formed by precipitation with $Ca(OH)_2$.

Slurries from both tanks are pumped to a filter for liquid-solid separations. The filtrate is fed to a hold tank, where it combines with the absorbent. The solids are discarded.

2.2.3 Gas Liquid Equilibria

The importance of gas-liquid equilibria in the process design is most significant in the sorption step, in the desorption column, and in the SO_2 stripping column.

The Sorption Step--

Kinetic data necessary for the sorption tower design are not available; however, the thermodynamic equilibria necessary to interpret mass transfer phenomena are known.

A 19.5 g/ℓ aluminum sulfite solution was found through bench-scale experiments to be the optimum concentration. The next step was to determine SO_2 vapor-liquid equilibrium data for this sorbent.

Results of the experimental part of the project are given in Figure 9. The abscissa shows the equilibrium amount of SO_2 (in weight percent) sorbed by a 19.5 g/ℓ aluminum sulfite solution. The left hand ordinate represents the partial pressure of SO_2 in torr in equilibrium with the liquid phase of a given composition. The partial pressure converted into volume percent SO_2 is indicated by the right hand coordinate.

The functional relationship of the two parameters is shown with the temperature as a parameter. The curved lines approximate the experimental results. The experimental data were fitted with an equation for computerization of the column design. The correlation found for the description of the vapor-liquid equilibria is:

$$\log p'' = 17.94 - \frac{3680}{T_{abs}} + 1.331 \frac{(X')^2}{(1-X')} \qquad (7)$$

p'' = partial pressure of SO_2 in torr over a 19.5 g/ℓ aluminum sulfite solution containing X' weight % SO_2.

X' = weight % SO_2 in a 19.5 g/ℓ aluminum sulfite solution.

T_{abs} = temperature at equilibrium in °Kelvin.

The equilibrium values derived from equation (7) are shown as straight lines in Figure 9. There are variations between calculated and experimental data at low vapor pressures. However, better agreement is obtained in the working range of interest which is about 1 volume %.

The dependence of the equilibrium partial pressure on the temperature at a given solution composition greatly affects energy consumption and, therefore, overall process cost.

The aluminum sulfite-based sorbent looks very favorable in this respect. The equilibrium pressure of a 19.5 g/ℓ aluminum sulfite solution containing 1 percent SO_2 is 0.03 mmHg at 20°C. A temperature increase to 70°C raises the partial pressure to 200 mmHg, making a difference of approximately 4 orders of magnitude. This is reflected in the heating and cooling requirements between the sorption and desorption step of the process.

The equilibrium data presented in Figure 9 can be used to calculate the SO_2 removal of an absorption column operating under equilibrium conditions. Input to this calculation is the SO_2 concentration of the incoming gas, the composition of the incoming liquor and the composition of the scrubbed gas. From this data, the increase in the SO_2 concentration in the absorption column bottoms, which is equivalent to the SO_2 pickup, can be calculated. One finds:

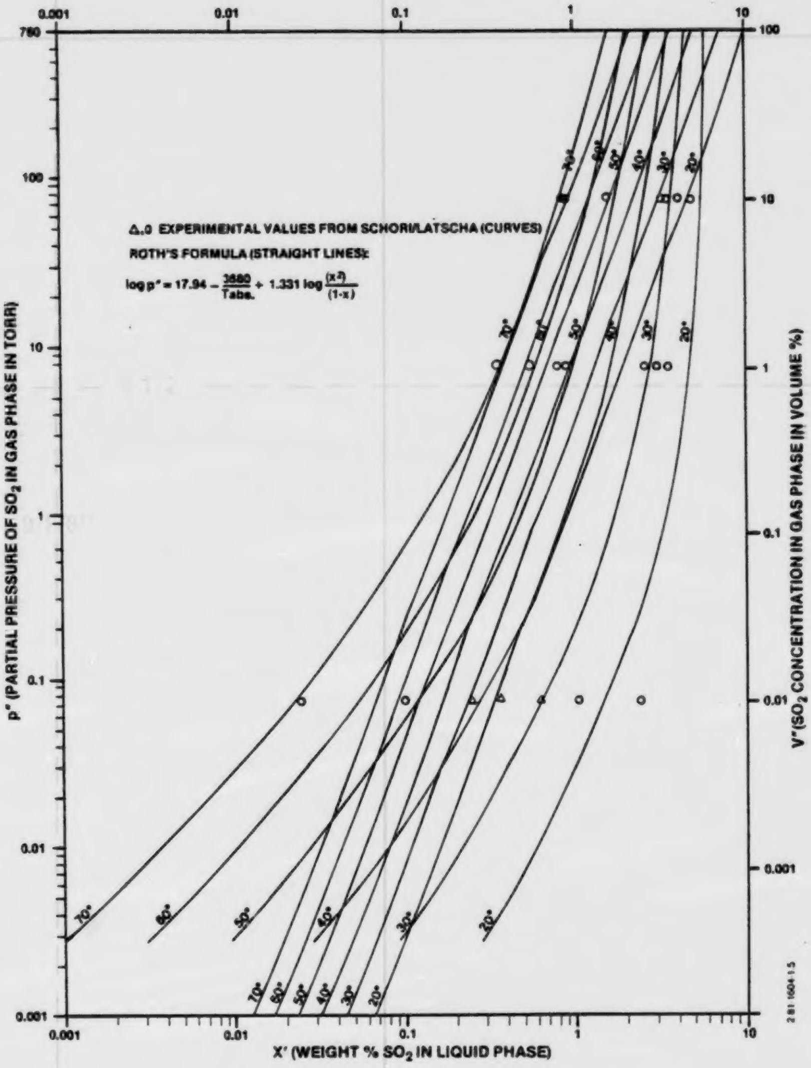

Figure 9. Gas-liquid equilibria of SO_2 in Al-sulfite solution (19.5 g/ℓ aluminum sulfite).

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$$\Delta X'_{SO_2}\,(A_2 - A_1) = \frac{1}{\frac{G'_{Abs}}{G''_{RG}}} \cdot \frac{M_{SO_2}}{M_{RG}} \left(V''_{SO_2} - \frac{100 \cdot P_{SO_2}{}'',\, A_2}{760} \right) \tag{8}$$

$\Delta X'_{SO_2}\,(A_2 - A_1)$ = Difference in weight % SO_2 of the incoming and outgoing scrubbing liquor.

$\frac{G'_{Abs}}{G'_{RG}}$ = L/G ratio; G'_{Abs} kg Absorbent/G'_{RG} kg gas

M_{SO_2} = Molecular weight of SO_2

M_{RG} = Molecular weight of raw gas

V''_{SO_2} = SO_2 concentration of incoming gas in volume %

$P_{SO_2}{}''$, A_2 = SO_2 partial pressure of scrubbed gas in Torr

The results of these calculations are given graphically in Figure 10. Temperature and SO_2 concentration of the gas are shown as parameters. The abscissa gives the SO_2 concentration of the liquor at the absorption tower entrance. The ordinate gives the increase of the sorption liquor in weight % SO_2.

Desorption Column--

The amount of SO_2 desorbed in the desorption tower must equal the amount picked up in the sorption section in order for the process to operate under steady-state conditions. The amount desorbed per kg solvent per pass can be influenced by several parameters, including:

- solvent temperature at tower inlet,
- vacuum applied to column, and
- amount of energy, mostly in the form of steam added.

The solvent temperature at the tower inlet can be varied through the steam input to the preceding heat exchanger. The ratio of the water vapor to SO_2 is influenced primarily by the tower temperature and secondarily, by the tower pressure. The amount of SO_2 desorbed in the column can be calculated by establishing an increment including:

- flow balance,
- mass balance for SO_2, and
- a heat balance.

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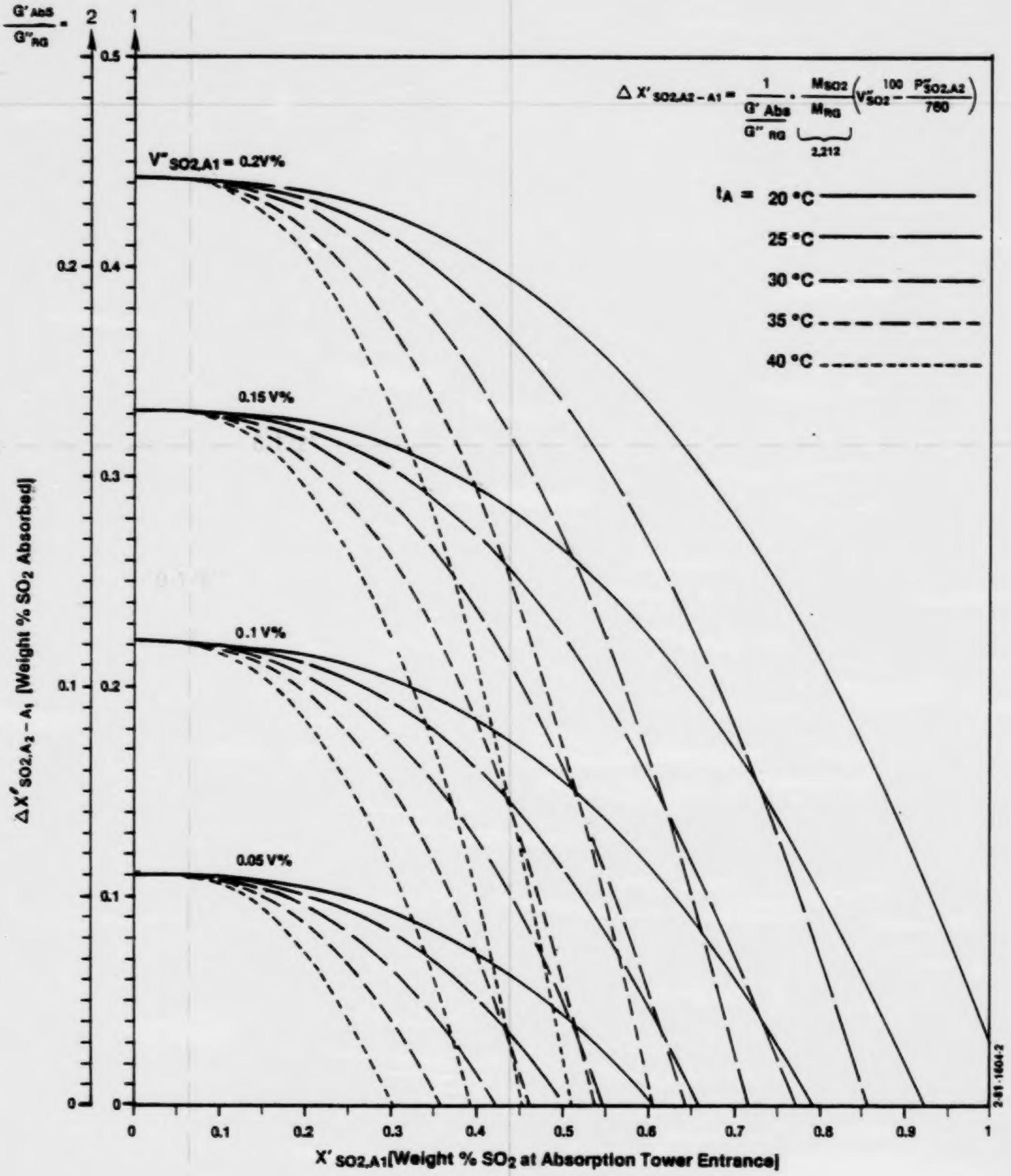

Figure 10. SO_2-absorbtion from a 19.5 g/ℓ aluminum sulfite solution. Reproduced with permission of Ciba-Geigy

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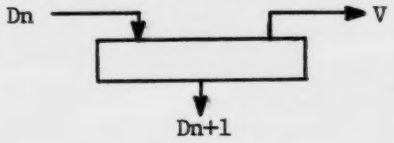
The resulting equation is then integrated over the length of the column, and over the temperature profile between inlet and outlet. The balances around a theoretical stage, n, can be formulated as follows:



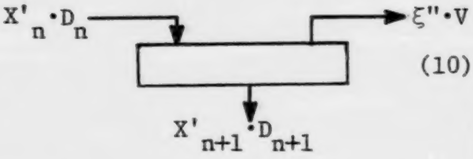
FLOW BALANCE:

$Dn = Dn{+}1 + V$ (9)

Dn = Liquor flow rate into theoretical stage n

$Dn{+}1$ = Liquor flow rate out of theoretical stage n

V = Vapor flow rate out of theoretical stage n



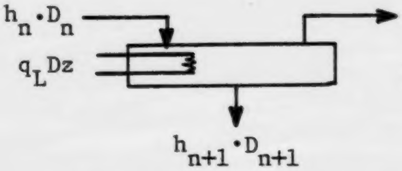
SO_2 BALANCE:

$X'_n \cdot D_n = X'_{n+1} \cdot D_{n+1} + \xi'' \cdot V$ (10)

$X'_n \cdot D_n$ = SO_2 flow rate in liquid phase into theoretical stage n

$X'_{n+1} \cdot D_{n+1}$ = SO_2 flow rate in liquid phase out of theoretical stage n

$\xi'' \cdot V$ = SO_2 flow rate in vapor phase out of theoretical stage n



ENERGY BALANCE:

$q_L \cdot Dz + h_n \cdot D_n = h_{n+1} \cdot D_{n+1} + H \cdot V$ (11)

$q_L \cdot Dz$ = enthalpy added to stage n by an external heat source

$h_n \cdot D_n$ = enthalpy of liquid entering stage n

$h_{n+1} \cdot D_{n+1}$ = enthalpy of liquid leaving stage n

$H \cdot V$ = enthalpy of gas phase leaving stage n

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By combining the three balances and integrating over the whole column, we find:

$$C_p(t_{D_1} - t_s) + \frac{\Delta q}{G'_{abs}} = \int_{X'_{SO_2D_2}}^{X'_{SO_2D_1}} \frac{HV_{H_2O}(1-\xi'') + HV_{SO_2}\xi'' - C_p(t_{D_1} - t_s)}{\xi''_{SO_2} - X'_{SO_2}} \cdot dX'_{SO_2} \qquad (12)$$

C_p = Specific heat of scrubber liquor

t_{D_1} = Temperature of incoming liquor

p = Pressure in desorption column

t_s = Boiling point of water at pressure p

$\Delta q/G'_{abs}$ = Heat/kg solvent added (e.g., steam)

$X'_{SO_2D_2}$ = % SO_2 in liquor at column exit

$X'_{SO_2D_1}$ = % SO_2 in liquor at column entrance

HV_{H_2O} = Specific heat of evaporation of water

ξ'' = Weight fraction SO_2 in gas phase

HV_{SO_2} = Specific heat of desorption of SO_2 gas from liquor

X'_{SO_2} = % SO_2 in liquor

The results of the numerical evaluation of equation (12) are shown in Figure 11 for a column pressure of 75 torr and in Figure 12 for a column pressure of 225 torr. The abscissas give the SO_2 concentration of the incoming liquor in weight % SO_2. The ordinates show the weight % SO_2 desorbed in the whole column. The effect of three temperatures (t_{D_1} = 80, 70, and 60°C) and three steam addition rates ($\Delta q/G'_{abs}$ = 10, 5, and 0 kilocalories per kg sorbent) were evaluated.

The sorption and desorption conditions must be balanced against each other in order to operate under steady-state conditions.

SO_2 Enrichment--

The SO_2-H_2O vapor phase leaving the desorption column is cooled in a condenser. The condenser effluent is fed to a stripping column, where the SO_2 is removed through air stripping. The equilibria in the stripping column are less complex than those in the sorption and desorption columns since the scale contains no dissolved salts.

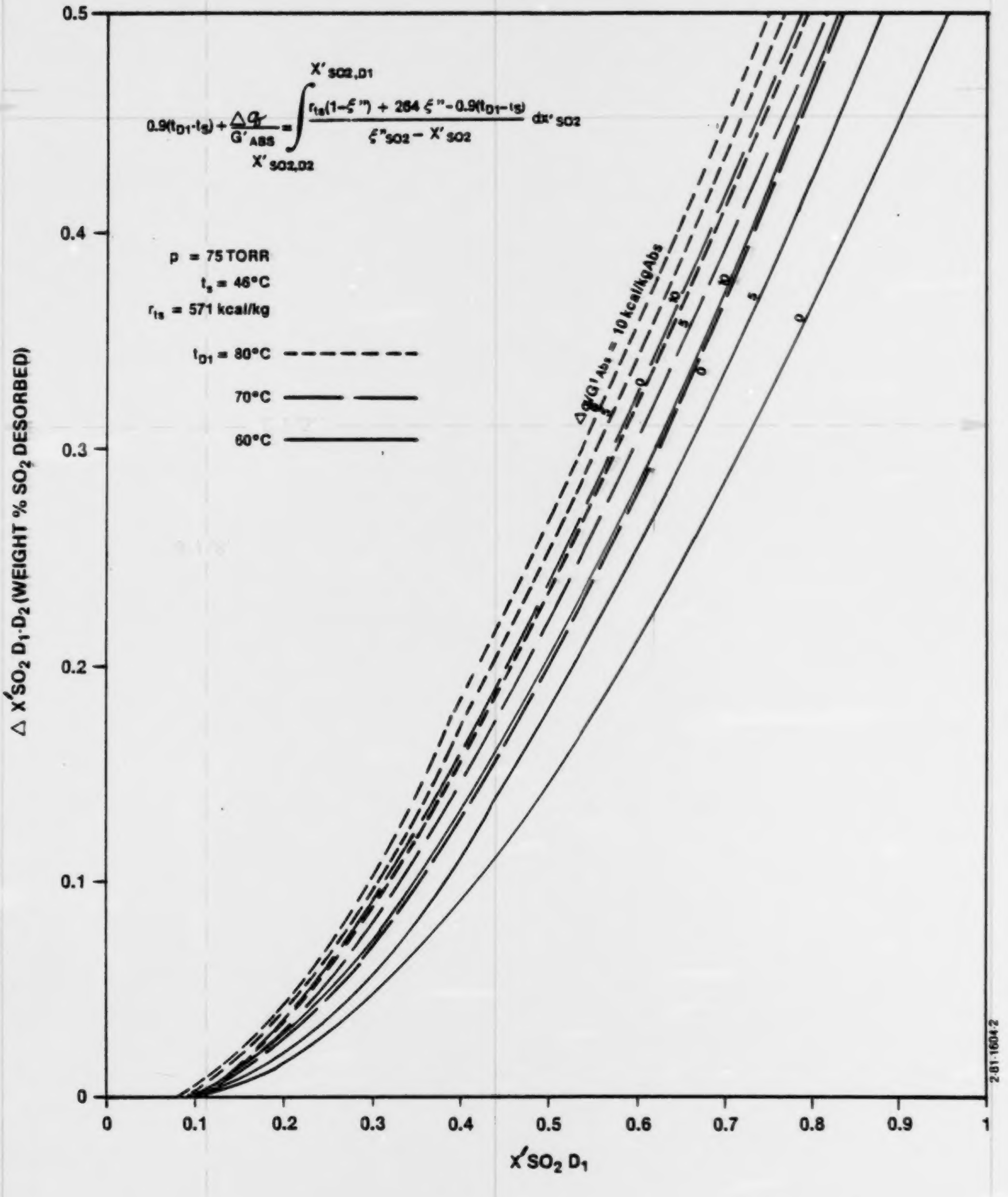

Figure 11. SO_2-desorbtion from a 19.5 g/ℓ aluminum sulfite solution. Reproduced with permission of Ciba-Geigy

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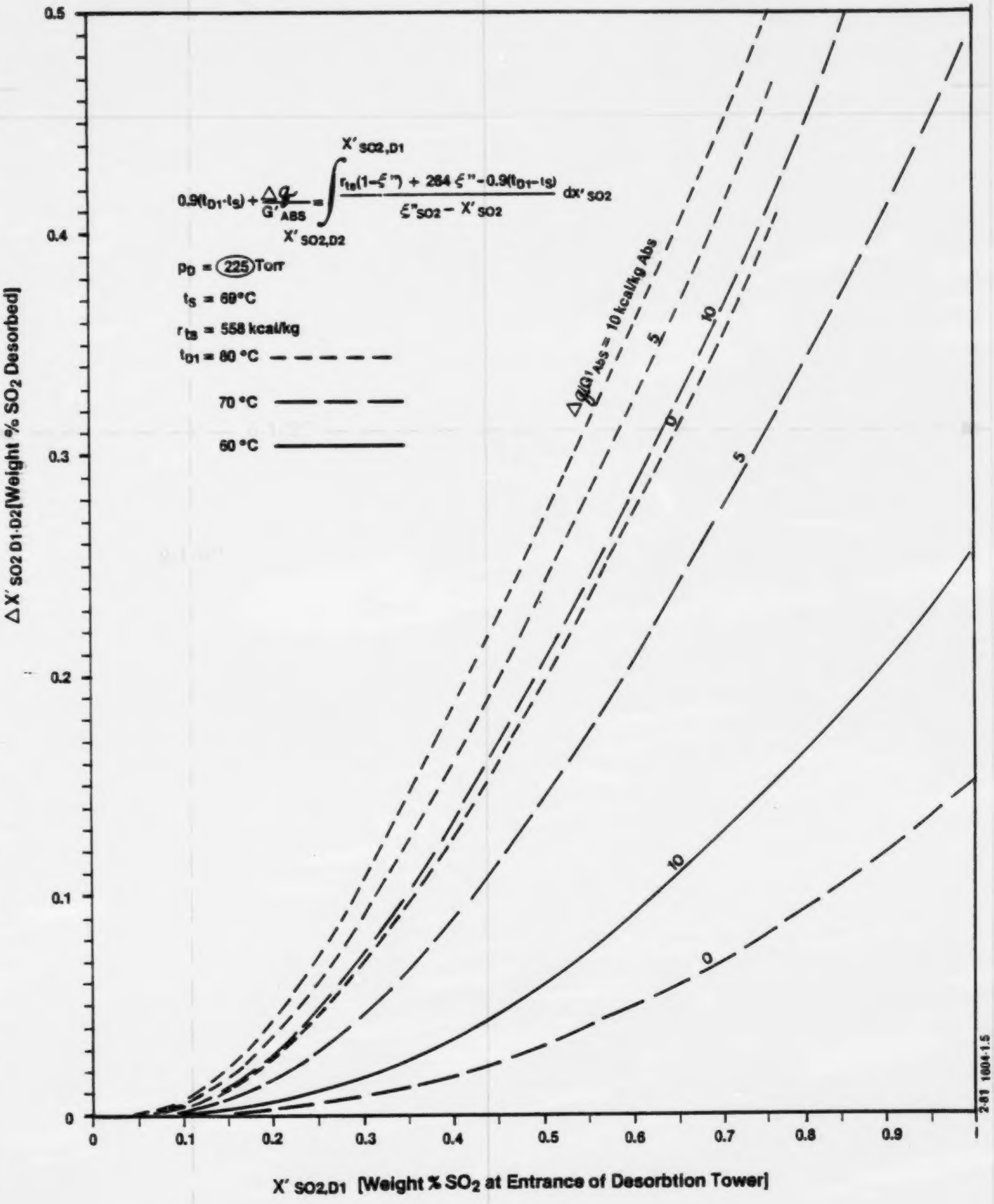

Figure 12. SO_2-desorbtion from a 19.5 g/ℓ aluminum sulfite solution. Reproduced with permission of Ciba-Geigy

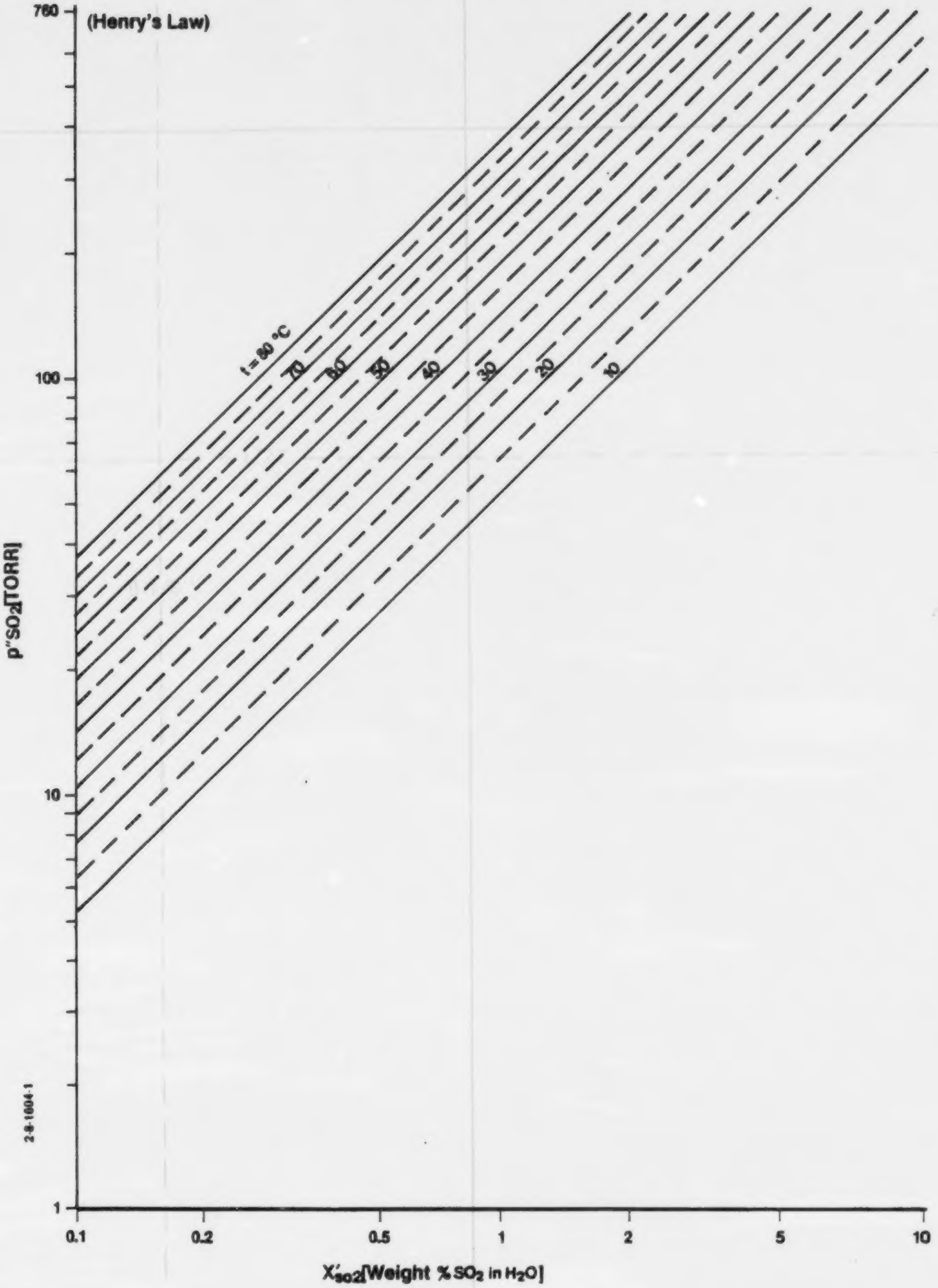

Figure 13. Gas-liquid equilibria for SO_2 in H_2O.
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The equilibrium SO_2 vapor pressures, as a function of solution composition, are represented in Figure 13. Temperature is given as a parameter.

2.2.4 Process Examples

Material and heat balances for two process examples are given below. The first example establishes balances for a gas stream with a high SO_2 concentration, and the second example establishes balances for a gas stream with a low SO_2 concentration. The calculations were normalized in both cases to 1000 Nm^3 gas treated. The examples described in this section have been successfully piloted on a 200 m^3/h scale.

Low Flow Rate, High SO_2 Concentration--
The numbers given in the following text are rounded from those in Figure 14, Example 1. Raw gas containing 1.9% SO_2 concentration enters the sorption tower, where it is contacted with a 19.5 g/ℓ aluminum sulfite solution with an SO_2 loading of $X'_{A_1} = 0.30$ weight % SO_2 at 40°C. The equilibrium SO_2 partial pressure is 611 ppm, according to the approximation (see Figure 2). This means that about 53 kg SO_2 are removed from the gas. Given a L/G ratio of 2 kg liquid/kg gas, the increase in the SO_2 concentration of the liquid is 2.01 weight %.

The two kg absorbents are heated from 40-64°C in the cross heat exchanger. This requires a heat input of 57197 kcal. This heat is extracted from the desorber effluent. The loaded absorbent is then heated from 64 to 80°C with steam. This requires an energy input of 2648 kg absorbent x $0.9 \frac{kcal}{kg°C}$ x 16°C = 38131 kcal.

The desorber pressure in this example is 225 torr. Enough steam is added to remove the 53 kg SO_2 sorbed in the sorption tower. The temperature of the desorption column adjusts itself through evaporation of water until the water equilibrium pressure equals 225 torr. The corresponding temperature is 69°C. The heat input necessary to remove 53 kg SO_2 under these conditions is 26480 kcal or 10 kcal/kg absorbent.

The sorbent leaves the desorber at 69°C with a SO_2 concentration of 0.30 weight % SO_2/kg liquid. It is cooled in the cross heat exchanger from 69 to 45°C. About 11916 kcal have to be extracted by the cooling water in the next heat exchanger to reach 40°C at the absorption column entrance.

The overall energy input is 38131 kcal to the heat exchanger (heating of the liquor from 64 to 80°C), plus 26480 kcal to the desorber to reach a SO_2 removal of 53 kg. This adds up to a total of 64600 kcal. This figure does not include pumping costs and other utility expenses.

The compositions and temperatures of the desorbed SO_2-H_2O vapor phase are shown in Figure 14.

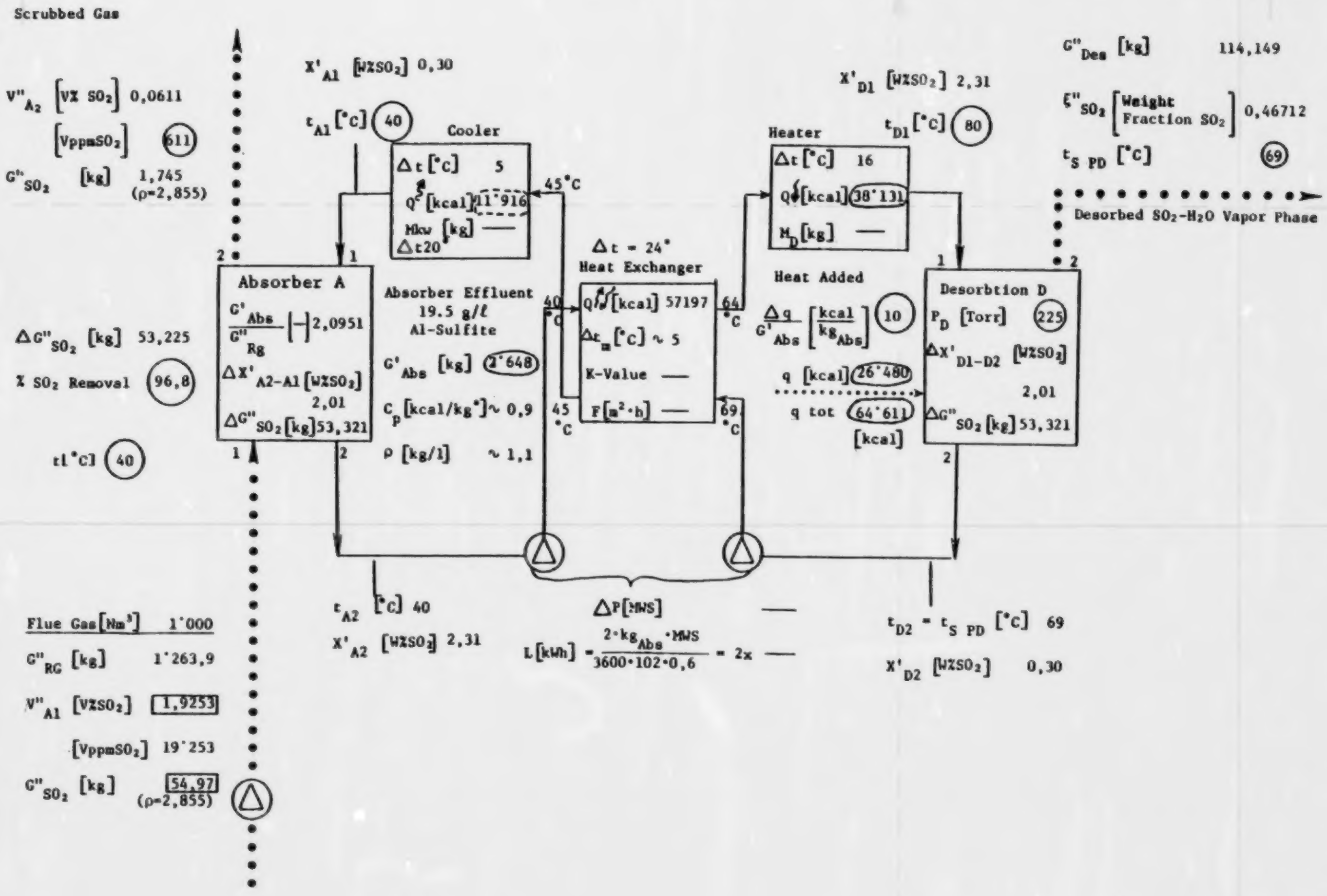
Scrubbed Gas
V"A2 [V% SO2] 0,0611
[VppmSO2] 611
G"SO2 [kg] 1,745 (ρ=2,855)
ΔG"SO2 [kg] 53,225
% SO2 Removal 96,8
t[°C] 40
X'A1 [W%SO2] 0,30
tA1 [°C] 40
Cooler
Δt [°C] 5
Q [kcal] 11'916
Mkw [kg] —
Δt20
45°C
Absorber A
G'Abs/G"Rg [—] 2,0951
ΔX'A2-A1 [W%SO2] 2,01
ΔG"SO2 [kg] 53,321
Absorber Effluent
19.5 g/ℓ
Al-Sulfite
G'Abs [kg] 2'648
Cp [kcal/kg°] ~ 0,9
ρ [kg/l] ~ 1,1
Δt = 24°
Heat Exchanger
Q [kcal] 57197
Δtm [°C] ~ 5
K-Value —
F [m²·h] —
40 °C
45 °C
64 °C
69 °C
Heater
Δt [°C] 16
Q [kcal] 38'131
MD [kg] —
X'D1 [W%SO2] 2,31
tD1 [°C] 80
Heat Added
Δq/G'Abs [kcal/kgAbs] 10
q [kcal] 26'480
q tot 64'611 [kcal]
Desorbtion D
PD [Torr] 225
ΔX'D1-D2 [W%SO2] 2,01
ΔG"SO2 [kg] 53,321
G"Des [kg] 114,149
ξ"SO2 [Weight Fraction SO2] 0,46712
tS PD [°C] 69
Desorbed SO2-H2O Vapor Phase
1
2
tA2 [°C] 40
X'A2 [W%SO2] 2,31
ΔP [MWS] —
L [kWh] = 2·kgAbs·MWS / 3600·102·0,6 = 2x —
tD2 = tS PD [°C] 69
X'D2 [W%SO2] 0,30
Flue Gas [Nm³] 1'000
G"RG [kg] 1'263,9
V"A1 [V%SO2] 1,9253
[VppmSO2] 19'253
G"SO2 [kg] 54,97 (ρ=2,855)

Figure 14. Example I - Heat and mass balance for a flue gas with high SO_2 concentration.

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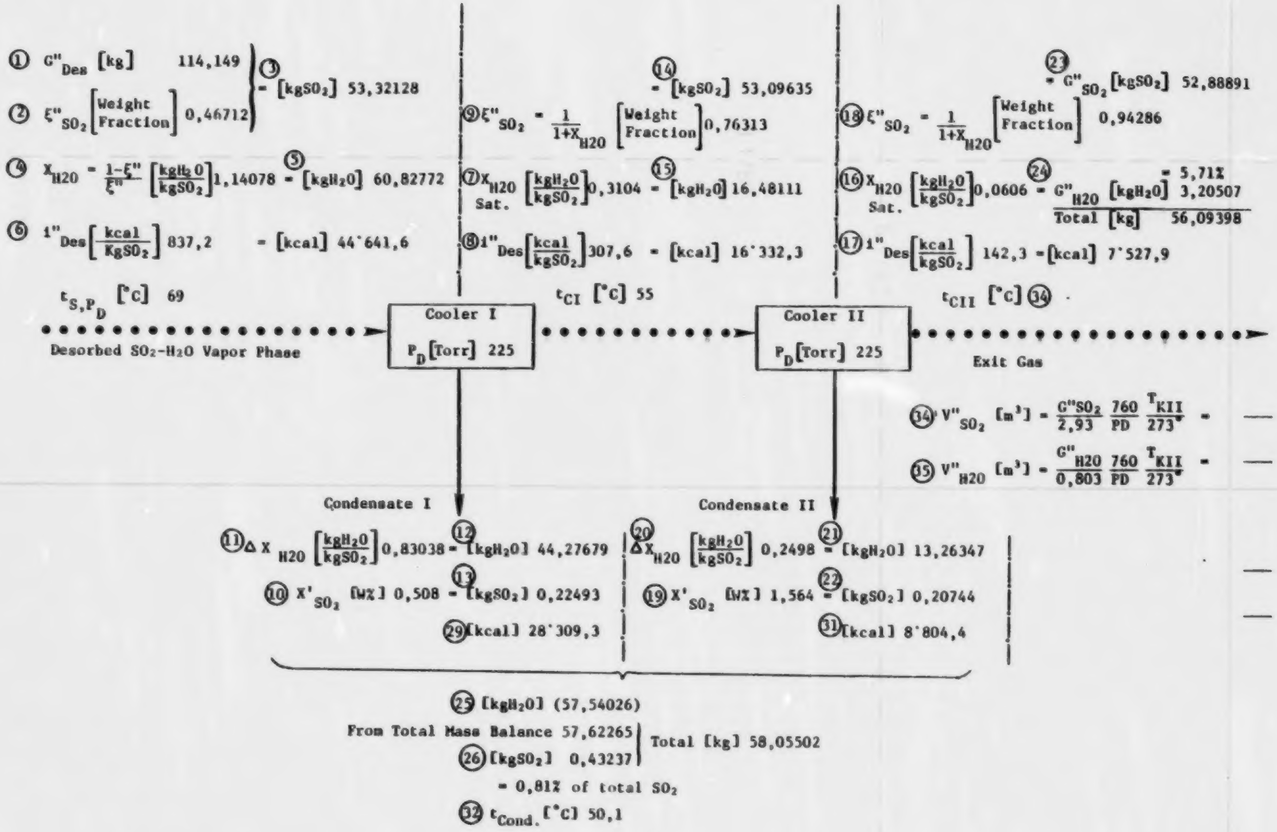
① G"Des [kg] 114,149
② ξ"SO2 [Weight Fraction] 0,46712
③ = [kgSO2] 53,32128
④ XH20 = (1-ξ")/ξ" [kgH2O/kgSO2] 1,14078
⑤ = [kgH2O] 60,82772
⑥ i"Des [kcal/KgSO2] 837,2 = [kcal] 44'641,6
tS,PD [°C] 69
Desorbed SO2-H2O Vapor Phase
Cooler I
PD [Torr] 225
⑭ = [kgSO2] 53,09635
⑨ ξ"SO2 = 1/(1+XH20) [Weight Fraction] 0,76313
⑦ XH20 Sat. [kgH2O/kgSO2] 0,3104
⑮ = [kgH2O] 16,48111
⑧ i"Des [kcal/kgSO2] 307,6 = [kcal] 16'332,3
tCI [°C] 55
Cooler II
PD [Torr] 225
㉓ = G"SO2 [kgSO2] 52,88891
⑱ ξ"SO2 = 1/(1+XH20) [Weight Fraction] 0,94286
⑯ XH20 Sat. [kgH2O/kgSO2] 0,0606
㉔ = G"H20 [kgH2O] = 5,71% 3,20507
Total [kg] 56,09398
⑰ i"Des [kcal/kgSO2] 142,3 = [kcal] 7'527,9
tCII [°C] ㉞
Exit Gas
㉞ V"SO2 [m³] = G"SO2/2,93 · 760/PD · TKII/273° = —
㉟ V"H20 [m³] = G"H20/0,803 · 760/PD · TKII/273° = —
Condensate I
⑪ Δ XH20 [kgH2O/kgSO2] 0,83038
⑫ = [kgH2O] 44,27679
⑩ X'SO2 [W%] 0,508
⑬ = [kgSO2] 0,22493
㉙ [kcal] 28'309,3
Condensate II
⑳ ΔXH20 [kgH2O/kgSO2] 0,2498
㉑ = [kgH2O] 13,26347
⑲ X'SO2 [W%] 1,564
㉒ = [kgSO2] 0,20744
㉛ [kcal] 8'804,4
㉕ [kgH2O] (57,54026)
From Total Mass Balance 57,62265
Total [kg] 58,05502
㉖ [kgSO2] 0,43237
= 0,81% of total SO2
㉜ tCond. [°C] 50,1

Figure 14. (Continued)

High Flow Rate, Low SO_2 Concentration--

The conditions in Figure 15, Example II are the same as in Example I. The sorbing liquor enters the sorption column at 40°C with an SO_2 loading of $X' = 0.28$ weight % SO_2. The SO_2 pickup of 0.38 weight % in the sorption column is, however, much smaller. L/G ratio is maintained at 2 kg absorbent/kg gas. The conditions for desorbing 10 kg SO_2 in the desorption section can be achieved by maintaining a liquor entrance temperature of 70°C, a pressure of 225 torr and a heat addition rate of 39660 kcal, which corresponds to 15 kcal/kg sorbent.

Total heat input is 14278 kcal to the heat exchanger preceding the sorption column and 39660 kcal to the column itself. This adds up to a total of 53938 kcal.

2.2.5 Removal Efficiency of the Process

The two examples described in the previous section indicate that the removal efficiency of the process decreases with decreasing SO_2 concentration in the incoming raw gas. This generally proves true if the sorbent loading, the sorbent temperature, the L/G ratio and the pressure in the desorption column are held constant. These conditions were met in the two examples.

The SO_2 removal efficiencies were 96.8 and 88.6 percent for raw gas containing 1.9 and 0.38 percent SO_2 respectively.

The energy requirements are comparable. In the first case, 38131 kcal are needed to heat the liquor from 64 to 80°C, and 26480 kcal heat input to the desorption column are required to achieve 53 kg SO_2 removal. This gave a total of 64611 kcal.

In the second case, only 14278 kcal are needed to heat the liquor from 64 to 70°C. However, a heat input of 39660 kcal to the column is necessary to remove 10 kg SO_2. Total heat requirement is therefore 53938 kcal.

Pumping costs are the same, since the L/G ratio did not change.

The principle observed in the above two cases holds generally true. The removal efficiency decreases with decreasing SO_2 content if sorption temperature, desorption pressure, and L/G ratio are kept constant. This correlation is quantified in Figure 16.

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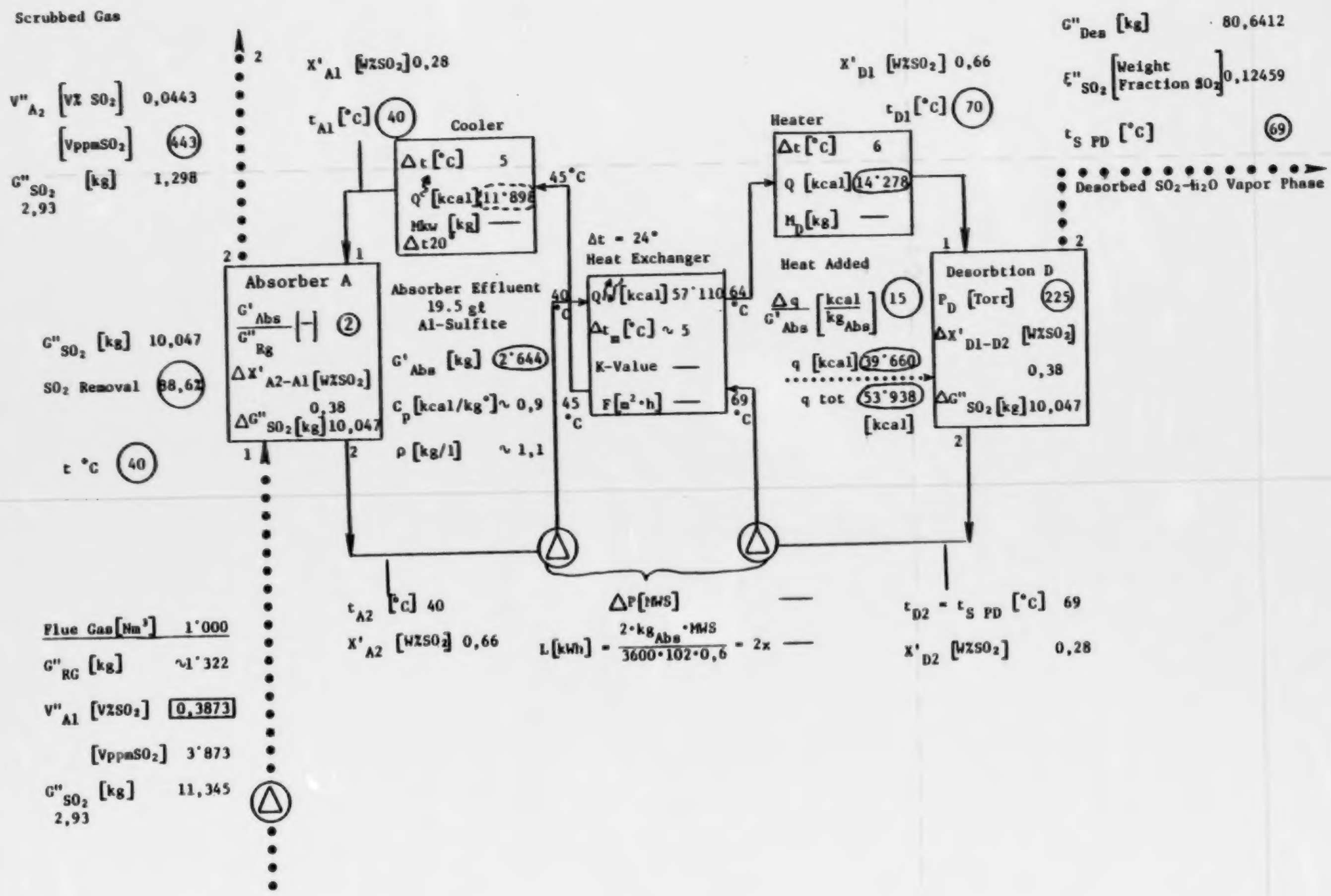
Scrubbed Gas
V"A2 [V% SO2] 0,0443
[VppmSO2] 443
G"SO2 [kg] 1,298
2,93
G"SO2 [kg] 10,047
SO2 Removal 88,62
t °C 40
Flue Gas [Nm³] 1'000
G"RG [kg] ~1'322
V"A1 [V%SO2] 0,3873
[VppmSO2] 3'873
G"SO2 [kg] 11,345
2,93
X'A1 [W%SO2] 0,28
tA1 [°C] 40
Cooler
Δt [°C] 5
Q [kcal] 11'898
Mkw [kg] —
Δt20
45°C
Absorber A
G'Abs / G"Rg [–] 2
ΔX'A2-A1 [W%SO2] 0,38
ΔG"SO2 [kg] 10,047
Absorber Effluent
19.5 gt
Al-Sulfite
G'Abs [kg] 2'644
Cp [kcal/kg°] ~ 0,9
ρ [kg/l] ~ 1,1
Δt = 24°
Heat Exchanger
Q [kcal] 57'110
Δtm [°C] ~ 5
K-Value —
F [m²·h] —
40 °C
45 °C
64 °C
69 °C
tA2 [°C] 40
X'A2 [W%SO2] 0,66
ΔP [MWS] —
L [kWh] = 2·kgAbs·MWS / 3600·102·0,6 = 2x —
Heater
Δt [°C] 6
Q [kcal] 14'278
MD [kg] —
X'D1 [W%SO2] 0,66
tD1 [°C] 70
Heat Added
Δq / G'Abs [kcal/kgAbs] 15
q [kcal] 39'660
q tot 53'938 [kcal]
Desorbtion D
PD [Torr] 225
ΔX'D1-D2 [W%SO2] 0,38
ΔG"SO2 [kg] 10,047
tD2 = tS PD [°C] 69
X'D2 [W%SO2] 0,28
G"Des [kg] 80,6412
ξ"SO2 [Weight Fraction SO2] 0,12459
tS PD [°C] 69
Desorbed SO2-H2O Vapor Phase
1
2

Figure 15. Example II - Heat and mass balance for a flue gas with low SO_2 concentration.

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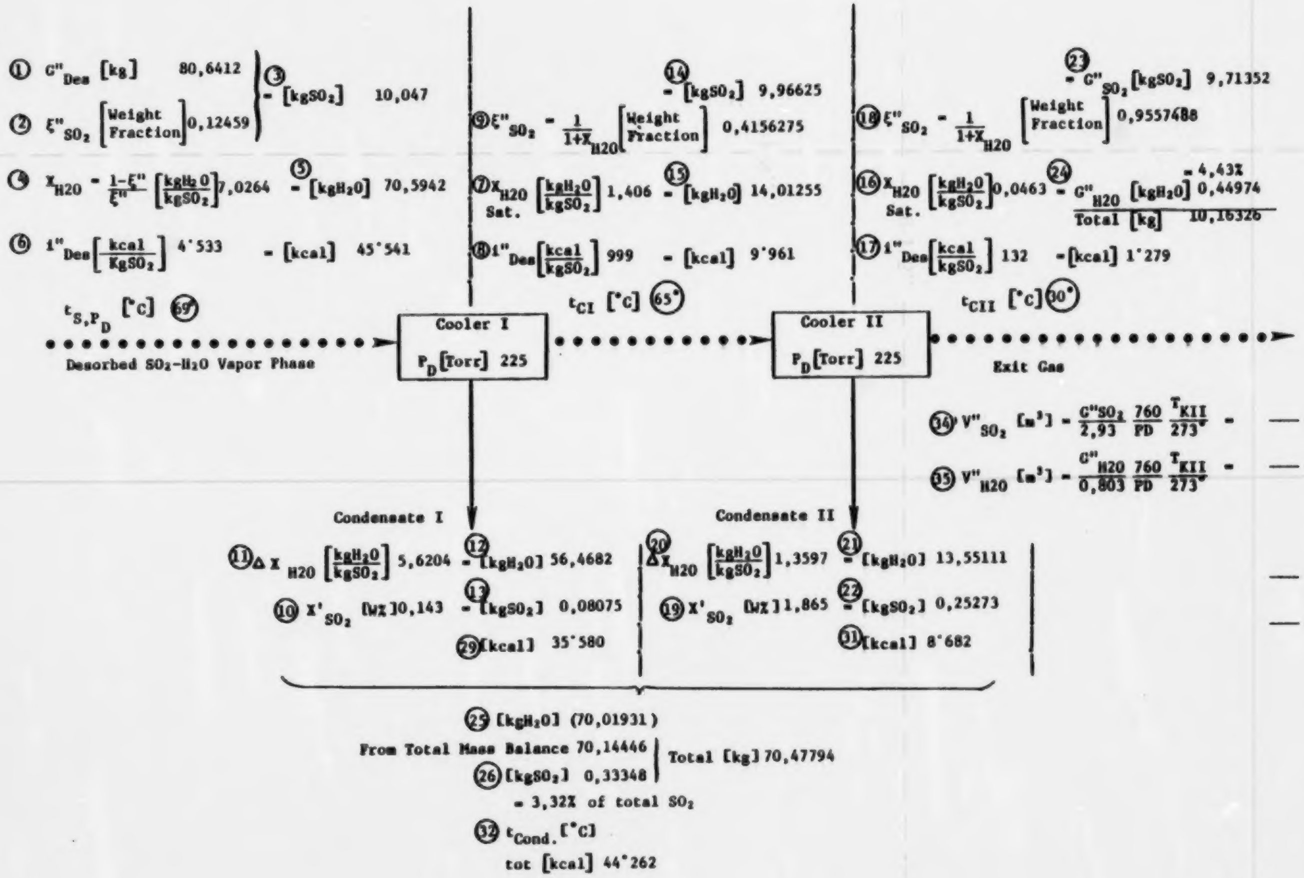
① G"Des [kg] 80,6412
② ξ"SO₂ [Weight Fraction] 0,12459
③ = [kgSO₂] 10,047
④ XH20 = (1-ξ")/ξ" [kgH₂O/kgSO₂] 7,0264
⑤ = [kgH₂O] 70,5942
⑥ i"Des [kcal/KgSO₂] 4'533
= [kcal] 45'541
tS,PD [°C] 69
Desorbed SO₂-H₂O Vapor Phase
Cooler I
PD [Torr] 225
⑨ ξ"SO₂ = 1/(1+XH20) [Weight Fraction] 0,4156275
⑭ = [kgSO₂] 9,96625
⑦ XH20 Sat. [kgH₂O/kgSO₂] 1,406
⑮ = [kgH₂O] 14,01255
⑧ i"Des [kcal/kgSO₂] 999
= [kcal] 9'961
tCI [°C] 65°
Cooler II
PD [Torr] 225
⑱ ξ"SO₂ = 1/(1+XH20) [Weight Fraction] 0,9557488
㉓ = G"SO₂ [kgSO₂] 9,71352
⑯ XH20 Sat. [kgH₂O/kgSO₂] 0,0463
㉔ = G"H20 [kgH₂O] 0,44974
= 4,43%
Total [kg] 10,16326
⑰ i"Des [kcal/kgSO₂] 132
= [kcal] 1'279
tCII [°C] 30°
Exit Gas
㉞ V"SO₂ [m³] = G"SO₂/2,93 · 760/PD · TKII/273° = —
㉟ V"H20 [m³] = G"H20/0,803 · 760/PD · TKII/273° = —
Condensate I
⑪ Δ X H20 [kgH₂O/kgSO₂] 5,6204
⑫ = [kgH₂O] 56,4682
⑩ X'SO₂ [Wt%] 0,143
⑬ = [kgSO₂] 0,08075
㉙ [kcal] 35'580
Condensate II
⑳ ΔXH20 [kgH₂O/kgSO₂] 1,3597
㉑ = [kgH₂O] 13,55111
⑲ X'SO₂ [Wt%] 1,865
㉒ = [kgSO₂] 0,25273
㉛ [kcal] 8'682
—
—
—
—
㉕ [kgH₂O] (70,01931)
From Total Mass Balance 70,14446
㉖ [kgSO₂] 0,33348
= 3,32% of total SO₂
Total [kg] 70,47794
㉜ tCond. [°C]
tot [kcal] 44'262

Figure 15. (Continued)

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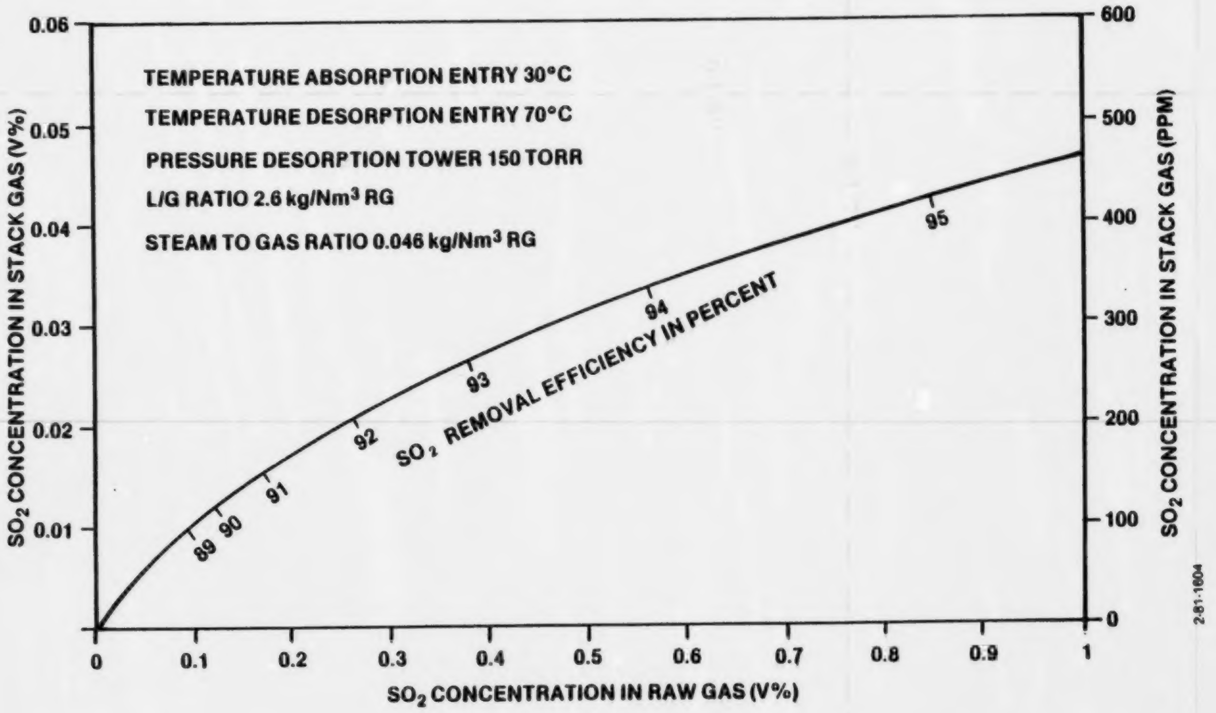

Figure 16. SO_2 removal efficiency of the Ciba-Geigy sorption-steam stripping process.

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SECTION 3

RESULTS OF BENCH-SCALE LIME SO_2 SCRUBBER TESTS

3.1 BENCH-SCALE LIME SO_2 SCRUBBER

A bench-scale lime scrubber was used by Radian to remove SO_2 from a small sample stream at the duct to the main stack of the Molycorp roasting facility in Washington, Pennsylvania. Scrubber solids were collected to quantify the amount of organic and inorganic impurities in the scrubber product and to evaluate the suitability of the solids for disposal or reuse. Additional tests were made to evaluate the scrubber performance.

A schematic of the bench-scale scrubber is shown in Figure 17. Gas was pumped from the main duct to the bubble contactor scrubber by a Teflon diaphragm pump. The gas contacted the slurry through a gas probe with several small holes in the tip. The cleaned gas was vented to the atmosphere after the scrubber.

The SO_2 scrubbing slurry was recirculated from the reaction tank to the scrubber by a peristaltic pump. Liquor was removed from the scrubber by gravity flow.

The pH was monitored in both the inlet and outlet slurry streams. These readings were then used to control the lime feed rate to the reaction tank. By adjusting the lime addition rate, the pH could be held at a fairly constant level.

To start the run, the scrubber liquor was spiked with pure gypsum crystals ($CaSO_4 \cdot 2H_2O$). The crystals provided sites for further crystal growth and diminished scale formation in the scrubber apparatus. A run typically lasted 2 to 3 hours. This length of time allowed the scrubber to produce an adequate sample for analysis.

Half way through the runs, it was determined that the liquid retention in the scrubber was too large. This became evident through slow pH response and limited pH reduction across the scrubber. The scrubber was modified to allow only one third of the original slurry retention for the remaining runs.

Inlet and outlet SO_2 measurements were made during each run by Reich tests. The SO_2 measurements are used to determine removals and effects of changing various operating parameters.

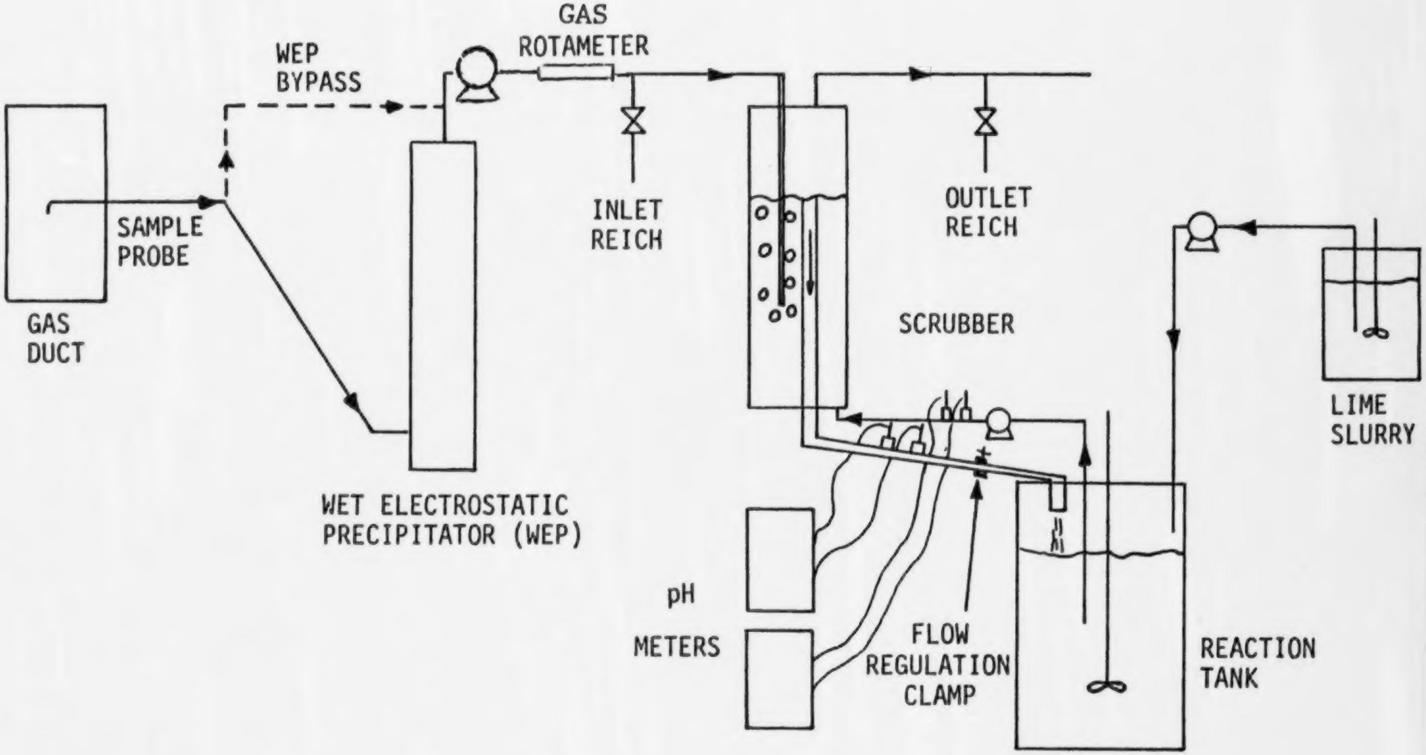
WEP
BYPASS
GAS
ROTAMETER
GAS
DUCT
SAMPLE
PROBE
INLET
REICH
OUTLET
REICH
SCRUBBER
LIME
SLURRY
WET ELECTROSTATIC
PRECIPITATOR (WEP)
pH
METERS
FLOW
REGULATION
CLAMP
REACTION
TANK

Figure 17. Bench-scale lime scrubber.

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The main emphasis of the bench-scale work was to collect a material which would represent the sludge from a lime FGD system if one were operating at Molycorp. After each run, the solids and liquid phases of the scrubbing liquor were separated; the solids were dried and the liquid was diluted with distilled water to reach the subsaturated region.

The analysis performed on the solid and liquid samples were SSMS and atomic absorption analysis for trace metals and gas chromatography for organics. The results of the analyses are presented in Section 3.2.

3.2 SCRUBBER PRODUCT CHARACTERIZATION

Bench-scale experiments were conducted on-site to prove the feasibility of lime wet scrubbing as a means of flue gas cleanup. The experiments and their results are summarized in Table 1. Parameters varied were:

- Liquid-gas contact time (probe depth)
- L/G ratio
- Lime feed rate (scrubber outlet pH)

The baseline conditions in Run 1 are used to compare the results from the other tests. While the inlet pH did vary somewhat in this run, the outlet pH was maintained at a fairly high level so that the Δ pH across the scrubber was small.

Experiments 7 and 8 were performed to gather solids under different scrubber conditions. Run 7 employed a WEP as a prescrubber and represents the major solids gathering effort along with Run 1. Run 8 did not use a WEP prescrubber but was conducted at a low scrubber outlet pH.

Runs 2,3 and 4 were performed using different gas probe depths. The SO_2 removal decreased with decreasing probe depth. This is due to a lower gas residence time. Removal was high during all the runs indicating that the high SO_2 driving force (i.e., high SO_2 concentrations in the flue gas) provided good mass transfer characteristics in the scrubber.

Runs 4, 5 and 6 were made at the same probe height but at different liquid feed rates. The outlet SO_2 concentration remained fairly constant over the three conditions. The volume of the scrubber was so great that the liquid feed rate was insignificant in comparison. For this reason the scrubber outlet pH remained constant regardless of the flow rate. Thus, the alkalinity furnished by the slurry coming into the scrubber was small compared to the available alkalinity already present in the scrubber. Furthermore, the scrubber alkalinity was more than sufficient to remove the SO_2 for such a small gas feed rate.

TABLE 1. EXPERIMENTAL CONDITIONS OF THE BENCH-SCALE LIME SCRUBBER TESTS

Run	Scrubber	Gas Rate (cfm)	Liquid Rate (ℓ/min)	Inlet pH	Outlet pH	$[SO_2]_{in}$ (ppm)	$[SO_2]_{out}$ (ppm)	% Removal	Probe Depth (cm below surface)
1	Large Scrubber	0.33	0.65	7-10	5-12	8120	153	98.1	30.5
2	Large Scrubber	0.33	0.74	8	5	9140	44	99.5	14.0
3	Large Scrubber	0.33	0.74	8	5	9140	51	99.4	8.9
4	Large Scrubber	0.33	0.74	8	4.8	9140	93	99.0	6.4
5	Large Scrubber	0.33	0.71	8	4.5	9140	98	98.9	6.4
6	Large Scrubber	0.33	0.49	8	4.8	9140	112	98.8	6.4
7	Large Scrubber + WEP	0.33	0.74	8.1	6.5	9140	49	99.5	17.1
8	Small Scrubber	0.33	0.22	7.8	3.4	10510	820	92.2	17.1
9	Small Scrubber	0.24	0.24	8.0	3.0	10400	1500	85.6	17.1
10	Small Scrubber	0.24	0.36	8.0	4.0	10400	392	96.2	17.1
11	Small Scrubber	0.24	0,96	8.0	5.0	10400	223	97.9	17.1

The consistently high removals obtained under the conditions described indicated that the scrubber was overdesigned. Therefore, a smaller, modified scrubber was used for Runs 9, 10 and 11. Table 1 shows the effect of scrubber liquor pH and liquid-to-gas ratio on the outlet SO_2 concentration using the smaller scrubber. The SO_2 outlet concentration increased significantly as the outlet pH of the scrubber blow down was decreased. This is to be expected since the available alkalinity is related to the pH.

Another goal of these experiments was the quantitation of trace impurities in the solid waste products. The following paragraph gives an estimate of the amount of gypsum produced in full-scale operation and describes the expected purity of the scrubber product.

During the June 21, 1978 test, the average rate of MoS_2 feed to the roaster was 1800 lb/hr, of which 219 lb/hr was found in the baghouse catch. Therefore an average of 1591 lb/hr of MoS_2 was actually converted to the oxide form. This corresponds to a sulfur feed rate of 632 lb/hr assuming that other sulfur containing compounds are insert or have a negligible contribution.

This gas flow rate at point 3 (Volume I, Figure 1) was measured to be 14,400 scf/min with a sulfur dioxide content of 7360 ppm (v/v). This translates to a discharge of 567 lb sulfur/hr. This is in very good agreement with the calculated input rate of 632 lb sulfur/hr.

This discharge rate will result in a production rate of 2590 lb gypsum/hr if lime/limestone based wet scrubbing is used for off-gas cleanup. This gypsum can contain impurities arising from three sources, namely from:

- the lime used as sorption agent,
- the gypsum seed crystals and
- from impurities contained in the scrubber gases.

Table 2 shows the survey analysis of the lime used in the experiment. It was the "Austin White Lime" sold for commercial applications. Table 3 presents the impurities in the scrubber end product and Table 4 with a WEP prescrubber. It is readily seen that the impurities of heavy metals are small in all three cases and that their level is the same. The use of a WEP prescrubber has no effect. The trace components are mainly introduced with lime.

A maximum contribution caused by the impurities present in the quench-scrubber exit gas can be calculated if we assume that all the impurities (see Table 1) end up in the gypsum. The results of these calculations are shown in Table 5 in the column "Calculated Maximum" Contribution of Flue Gas. It is obvious from the data shown in this table, that the quantity of trace constituents introduced by the lime, correlate much better with the impurities in the scrubber product than the impurities present in the humidifier scrubber exit gases. This indicates that the origin of the impurities is the lime.

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TABLE 2. SSMS ANALYSIS OF LIME USED IN SO_2 SCRUBBING TESTS (SAMPLE NO. M-095)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	7	Terbium		Ruthenium		Vanadium	12
Thorium		Gadolinium		Molybdenum	10	Titanium	5
Bismuth		Europium		Niobium	0.8	Scandium	1
Lead	1	Samarium		Zirconium	4	Calcium	>1000
Thallium		Neodymium	1	Yttrium	2	Potassium	120
Mercury	NR	Praseodymium	0.3	Strontium	430	Chlorine	28
Gold		Cerium	3	Rubidium	0.4	Sulfur	62
Platinum		Lanthanum	2	Bromine	1	Phosphorus	86
Iridium		Barium	10	Selenium	1	Silicon	>1000
Osmium		Cesium		Arsenic	3	Aluminum	>200
Rhenium		Iodine		Germanium		Magnesium	>1000
Tungsten		Tellurium		Gallium	1	Sodium	26
Tantalum		Antimony	0.7	Zinc	9	Fluorine	*560
Hafnium		Tin		Copper	3	Oxygen	NR
Lutetium		Indium		Nickel	8	Nitrogen	NR
Ytterbium		Cadmium		Cobalt	0.4	Carbon	NR
Thulium		Silver	0.7	Iron	>1000	Boron	0.8
Erbium		Palladium		Manganese	100	Beryllium	
Holmium		Rhodium		Chromium	9	Lithium	1
Dysprosium						Hydrogen	NR

NR - Not Reported
All elements not detected <0.3 ppm weight
INT - Interference *Heterogeneous

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TABLE 3. SSMS ANALYSIS OF LIME SCRUBBING END PRODUCT NO PRESCRUBBER USED (SAMPLE NO. M-017)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	≤2	Terbium		Ruthenium		Vanadium	5
Thorium		Gadolinium		Molybdenum	5	Titanium	62
Bismuth		Europium		Niobium	0.5	Scandium	0.2
Lead	1	Samarium		Zirconium	3	Calcium	>1000
Thallium		Neodymium		Yttrium	2	Potassium	87
Mercury	NR	Praseodymium	0.3	Strontium	150	Chlorine	53
Gold		Cerium	2	Rubidium	≤ 0.1	Sulfur	>1000
Platinum		Lanthanum	2	Bromine	≤ 0.6	Phosphorus	91
Iridium		Barium	6	Selenium	9	Silicon	>1000
Osmium		Cesium		Arsenic	2	Aluminum	≥210
Rhenium		Iodine	0.7	Germanium	5	Magnesium	>1000
Tungsten		Tellurium		Gallium	0.3	Sodium	18
Tantalum		Antimony		Zinc	35	Fluorine	*190
Hafnium		Tin		Copper	6	Oxygen	NR
Lutetium		Indium	STD	Nickel	29	Nitrogen	NR
Ytterbium		Cadmium		Cobalt	3	Carbon	NR
Thulium		Silver	0.9	Iron	< 1000	Boron	0.5
Erbium		Palladium		Manganese	22	Beryllium	
Holmium		Rhodium		Chromium	1	Lithium	0.6
Dysprosium						Hydrogen	NR

NR - Not Reported
All elements not detected <0.3 ppm weight
INT - Interference *Heterogeneous

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TABLE 4. SSMS ANALYSIS OF LIME SCRUBBING END PRODUCT WITH WEP PRESCRUBBER IN USE (SAMPLE NO. M-098)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	≤2	Terbium		Ruthenium		Vanadium	7
Thorium		Gadolinium		Molybdenum	2	Titanium	50
Bismuth		Europium		Niobium	≤ 0.4	Scandium	≤ 0.2
Lead	1	Samarium		Zirconium	3	Calcium	1000
Thallium		Neodymium	0.8	Yttrium	5	Potassium	87
Mercury	NR	Praseodymium	0.3	Strontium	150	Chlorine	80
Gold		Cerium	2	Rubidium	≤ 0.1	Sulfur	> 1000
Platinum		Lanthanum	1	Bromine	≤ 1	Phosphorus	91
Iridium		Barium	6	Selenium	9	Silicon	> 1000
Osmium		Cesium		Arsenic	3	Aluminum	≥ 210
Rhenium		Iodine		Germanium	3	Magnesium	> 1000
Tungsten		Tellurium		Gallium	0.5	Sodium	27
Tantalum		Antimony		Zinc	35	Fluorine	≈ 250
Hafnium		Tin		Copper	7	Oxygen	NR
Lutetium		Indium	STD	Nickel	9	Nitrogen	NR
Ytterbium		Cadmium		Cobalt	3	Carbon	NR
Thulium		Silver	0.6	Iron	> 1000	Boron	4
Erbium		Palladium		Manganese	36	Beryllium	
Holmium		Rhodium		Chromium	2	Lithium	0.7
Dysprosium						Hydrogen	NR

NR - Not Reported
All elements not detected <0.3 ppm weight
INT - Interference *Heterogeneous

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TABLE 5. TRACE CONSTITUENTS IN LIME AND LIME SCRUBBER PRODUCTS (ppm)

Element	Measured Impurities In Lime	Gypsum Seeds	Product Without Pre-Scrubber	Product With Pre-Scrubber	Calculated Maximum Contribution of Flue Gas	Liquor Without Pre-Scrubber µg/ml	Liquor With Pre-Scrubber µg/ml	Interim Primary Drinking Water Standards µg/ml	Irrigation Water Standards µg/ml
Arsenic	1	<1	1	1	.3	.005	.005	.05	1.0
Lead	<1	1.8	1	1	6	<.02	<.02	0.05	5.0
Molybdenum	7	9	9	9	39	< .5	<.5	-	0.01
Mercury	<.005	<.005	<.005	<.005	.01	<.005	<.005	.002	-
Selenium	.3	.5	1	.5	31	<.005	<.005	.01	0.02
Bismuth	<.01	<.01	<.01	<.01	.15	<.005	<.005	-	-
Antimony	.1	<1	1	1	.02	<.005	<.005	-	-
Cadmium	<.01	<.01	<.01	<.01	<.1	<.005	<.005	0.01	0.01
Silver	.05	.4	.07	.09	.3	<.005	<.005	0.05	-
Zinc	5	20	25	19	.2	<.03	<.03	-	2.0
Nickel	4	5	15	5	<.04	<.05	<.05	-	0.2
Copper	1.5	1.9	3	2.2	.6	<.05	<.05	-	0.2
Manganese	72	93	70	95	.5	<.05	<.05	-	0.2
Iron	1500	1100	1600	1550	2.8	<.05	<.05	-	5.0
Rhenium	ND								

ND-Not determined

The scrubber liquors were also analyzed for the 15 elements of interest. The results obtained with and without prescrubber are compared with maximum concentrations allowed in drinking water and irrigation water. The limits are in no case exceeded. A higher concentration buildup may, however, be possible in scrubber solutions produced under long-term steady-state conditions. The degree of buildup needs to be checked in long-term pilot plant studies.

SECTION 4

FLUE GAS DESULFURIZATION ALTERNATIVES AND CONCEPTUAL DESIGN OF A LIMESTONE FGD SYSTEM

Several flue gas desulfurization (FGD) technologies developed for use in the utility industry have potential application for control of sulfur dioxide emissions from nonferrous smelters. However, smelter offgases have certain characteristics which may affect the applicability of existing FGD technology including:

- SO_2 concentrations greater than 5,000 ppm,
- variable SO_2 concentrations,
- SO_3 concentrations up to 100 ppm,
- metal fumes in the offgas, and
- organics in the offgas.

Molybdenum roasting operations at Molycorp's Washington, Pennsylvania smelter produce an offgas with about 7,000 ppm SO_2 and 100 ppm SO_3. In the near future Molycorp will be required by the State of Pennsylvania to apply some type of SO_2 control to their roaster offgas. The various FGD technologies which might be applied at Molycorp and a preliminary process design and cost estimate for a limestone system are presented in this section of the report.

4.1 FGD PROCESS ALTERNATIVES

The following sections describe several different FGD process alternatives and discuss their applicability to Molycorp's high SO_2 offgas. Major emphasis was given to the lime/limestone slurry, dual alkali, magnesia slurry, and Wellman-Lord systems. These systems represent the most developed FGD technology available. Other systems such as the Sulf-X, Endako, Chiyoda Thoroughbred 121, buffered citrate, sodium carbonate throwaway, Dowa aluminum sulfate, and sorption/steam stripping are also examined with respect to their applicability to the molybdenum roaster offgas.

Estimates of stream flows and equipment requirements for Molycorp are included for the first four of the process alternatives mentioned above. The design basis for these determinations was:

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Gas flow rate - 28,800 acfm @ 110°F, 14.16 psia

Inlet SO_2 concentration - 7,460 ppm (dry)

SO_2 removal - 95 percent

SO_2 oxidation - 15 percent

4.1.1 Lime/Limestone Slurry Process

The lime/limestone slurry FGD process has experienced the greatest extent of application of any FGD process in the U.S. today. This process is attractive because the makeup lime/limestone is inexpensive enough to allow the waste product to be disposed of economically. Generally a limestone throwaway system is the economic choice over lime for most utility applications. Lime systems are usually slightly more expensive over the life of the plant due to the cost of calcining limestone to produce lime. The major drawbacks for either system are the disposal of large quantities of by-product waste sludge in an environmentally sound manner and the potential for formation of chemical scale within the process.

Process Description--

The lime/limestone FGD process uses a slurry containing calcium hydroxide [$Ca(OH)_2$] or calcium carbonate ($CaCO_3$) to absorb SO_2 in a wet scrubber. After absorption calcium sulfite and sulfate crystals are precipitated in a reaction tank. The majority of this slurry is recycled to the scrubber. A portion of the reaction tank slurry is sent to a solid/liquid separator where the solids are concentrated and removed from the system. The waste solids are generally disposed of by ponding or landfill. Figure 18 shows a simplified limestone scrubbing process flow diagram.

The basic processing steps of a lime/limestone wet scrubbing system can be divided into three areas: SO_2 absorption, solids precipitation and dissolution, and solids separation and disposal.

A 10-15 weight percent slurry is fed to the scrubber where gaseous SO_2 is absorbed in the liquor forming sulfurous acid. Reaction of the sulfurous acid with alkaline species in the liquor reduces the equilibrium SO_2 partial pressure exerted by the liquor which allows more SO_2 to be absorbed. Oxidation of some of the abosrbed sulfite ions may occur in the liquor which will result in the formation of sulfate ions.

Spent slurry from the scrubber is sent to a reaction tank where limestone or lime is added. The reaction tank is sized to provide adequate time for both additive dissolution and calcium sulfite and sulfate precipitation. The solids which are formed may include a calcium sulfite-sulfate solid solution and/or gypsum ($CaSO_4$). If too little reaction time is provided, nucleation of calcium sulfite or calcium sulfate may occur in the scrubber which will cause chemical scale to be deposited on scrubber internals. Scaling may

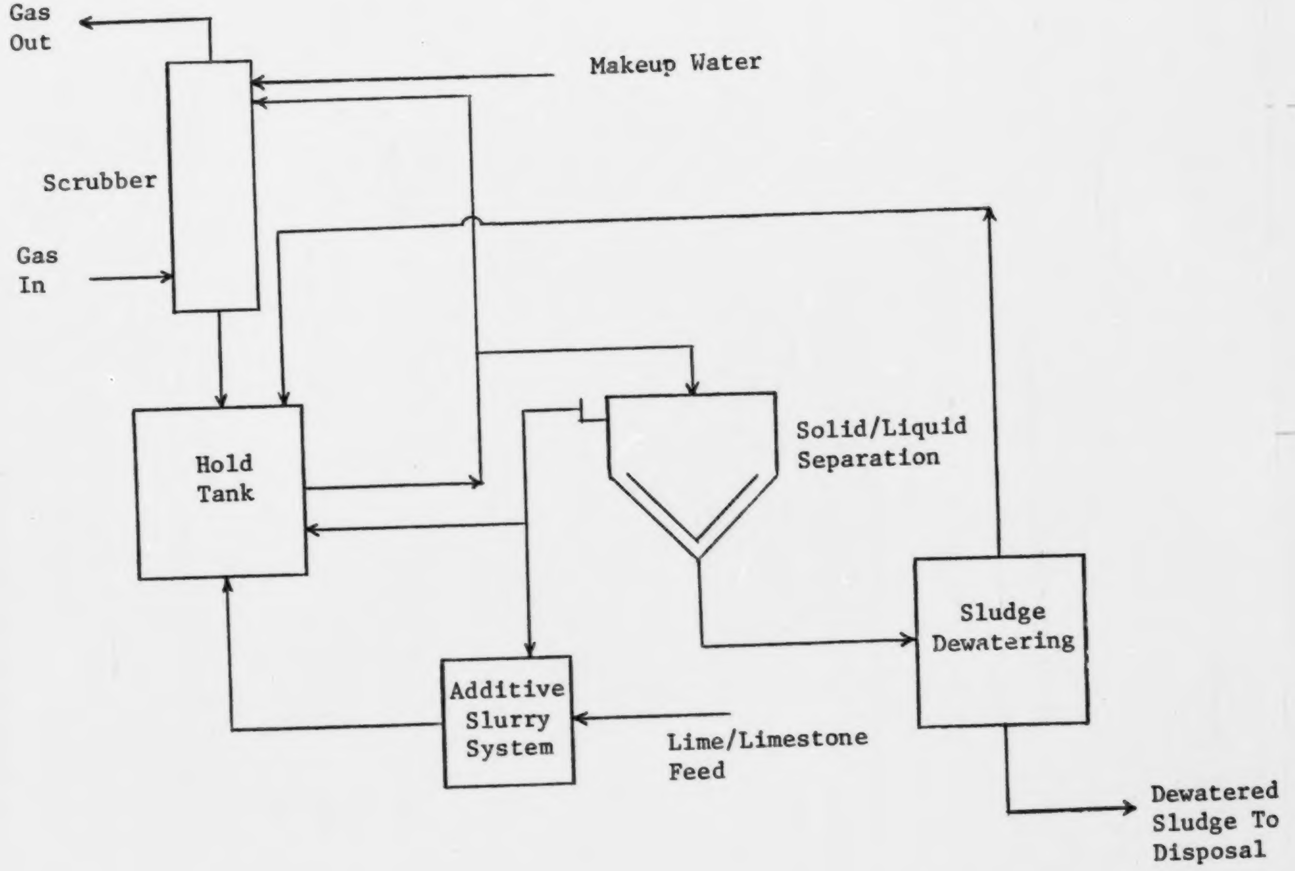

Gas
Out
Makeup Water
Scrubber
Gas
In
Hold
Tank
Solid/Liquid
Separation
Sludge
Dewatering
Additive
Slurry
System
Lime/Limestone
Feed
Dewatered
Sludge To
Disposal

Figure 18 . Simplified lime/limestone wet scrubbing process.

result in increased maintenance costs. Sometimes inadequate time may also result in high limestone consumption rates.

The overall reactions for limestone and lime systems are shown in Equations 23 through 26.

Limestone System

$$CaCO_3(s) + SO_2 + x/2\ O_2 + \tfrac{1}{2}H_2O \rightleftharpoons [(1-x)\ CaSO_3 \cdot x\ CaSO_4] \cdot \tfrac{1}{2}H_2O(s) + CO_2(g) \qquad (23)$$

$$CaCO_3(s) + SO_2 + \tfrac{1}{2}O_2 + 2H_2O \rightleftharpoons CaSO_4 \cdot 2H_2O(s) + CO_2(g) \qquad (24)$$

Lime System

$$Ca(OH)_2(s) + SO_2 + x/2\ O_2 + \rightleftharpoons [(1-x)CaSO_3 \cdot x\ CaSO_4] \cdot \tfrac{1}{2}H_2O(s) + \tfrac{1}{2}H_2O \qquad (25)$$

$$Ca(OH)_2(s) + SO_2 + \tfrac{1}{2}\ O_2 + H_2O \rightleftharpoons CaSO_4 \cdot 2H_2O(s) \qquad (26)$$

The calcium sulfite/sulfate solids formed in the system are removed from the reaction tank in a bleed stream. A dewatering step is then performed to minimize handling problems and reduce the volume of material required for landfill. Depending on the physical properties of the solids produced, a thickening device such as a clarifier or centrifuge can be used to increase the solids content to about 25-50 weight percent. Additional dewatering to 50-80 percent solids can be achieved by vacuum filtration. For systems with on-site pond disposal, the hold tank bleed stream can be pumped directly to the pond area. Pond overflow is then returned to the system to maintain the water balance.

One variation of the lime/limestone system is to use force oxidation. Oxygen in the form of air is sparged into the reaction tank to oxidize all sulfite species to sulfate. The resulting sludge is generally easier to dewater and landfill. In addition, it may be possible to sell the gypsum product for wallboard. However, natural supplies of gypsum are such that a potential buyer may be difficult to locate (18).

Applicability to Smelter/Roaster Offgases--
High SO_2 concentrations characteristic of smelter/roaster offgases may present a problem to limestone wet scrubbing. Getting the required removal at reasonable liquid-to-gas (L/G) ratios is a major concern. Sludge disposal may also be a problem if trace elements in the roaster offgas leave the FGD process in the sludge. The presence of these trace elements could cause the sludge to be designated a hazardous waste. Current proposed regulations require expensive disposal techniques for wastes which are deemed hazardous.

The limestone system has generally been found to be relatively inexpensive compared to other FGD processes at least for utility applications. Operating costs and capital expenditures for application in a smelter offgas could increase significantly, however, due to the high liquid rates. Land requirements for sludge disposal may also limit the use of this or any other throwaway process.

Equipment Sizing--

The major design parameters of lime/limestone FGD systems are the SO_2 absorption capacity of the liquor, the approach to solid/liquid equilibrium in the reaction tank, liquid-to-gas (L/G) ratio and the residence time of the solids in the reaction tank. The L/G which will determine the SO_2 removal capability of the system is a function of the liquid phase alkalinity (the ability of the liquid to absorb SO_2). The available alkalinity is dependent on the amount of dissolved solids and is increased by the presence of species such as magnesium and sodium.

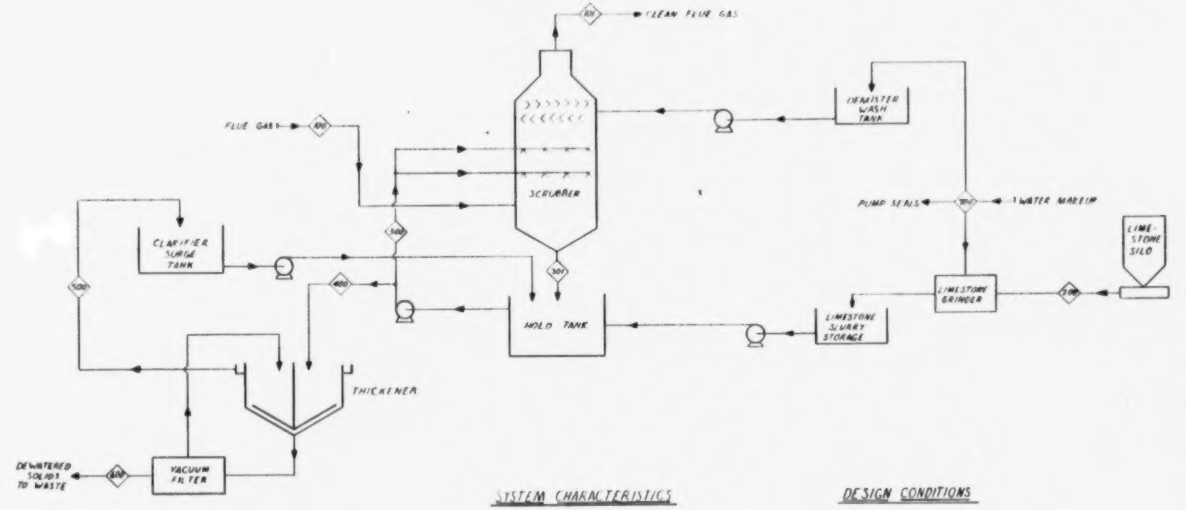
The reaction tank size is dependent on two variables: (1) calcium sulfite/sulfate solids precipitation rate and (2) calcium carbonate/calcium hydroxide dissolution rate. Calcium sulfate precipitation is a major concern. If the relative saturation of calcium sulfate is too high (i.e., greater than 1.4), gypsum scale which plugs equipment is formed. The size of the reaction tank is calculated from the kinetic equations describing precipitation and dissolution rates. In utility boiler applications, solids residence times on the order of 1,000 minutes are found under normal conditions.

The weight percent solids and reagent stoichiometry are also primary design parameters. Lime/limestone systems operate with slurry solid contents ranging from 10 to 15 weight percent solids and at reagent stoichiometries (with respect to SO_2 removal) of around 1.0-1.05 for lime and 1.05 to 1.3 for limestone. The solids in the slurry provide sites for crystal growth and a source of soluble alkalinity in the scrubber. Therefore, at higher solids contents there is greater potential for precipitation and SO_2 removal. Stoichiometry is set by removal and system design, with the stoichiometry as low as possible to minimize reagent loss. Even though a higher SO_2 removal requirement may require a higher stoichiometry, process design can still minimize reagent losses. A double loop scrubbing system design has been shown to be effective in lowering reagent stoichiometries in limestone scrubbing systems.

An estimate of the stream flows and equipment requirements for Molycorp are given in Figure 19. A more detailed discussion of the conceptual design of a limestone FGD system is presented in Section 4.2 of this report.

4.1.2 Dual Alkali Process

Several vendors in the U.S. have developed alkali systems. These include Combustion Equipment Associates (non Thyssen/CEA Environmental System) and Arthur D. Little (CEA/ADL), FMC Corporation, General Motors, Zurn Inudstries, and Buell/Envirotech (non General Electric).


FLUE GAS
100
101
CLEAN FLUE GAS
SCRUBBER
DEMISTER WASH TANK
PUMP SEALS
700
WATER MAKEUP
LIME-STONE SILO
210
LIMESTONE GRINDER
LIMESTONE SLURRY STORAGE
HOLD TANK
301
300
400
CLARIFIER SURGE TANK
500
THICKENER
VACUUM FILTER
600
DEWATERED SOLIDS TO WASTE

STREAM NUMBER	210	300	301	400	500	600	700
TOTAL FLOW lb/hr	3000	$4,61 \times 10^{6}$	$4,61 \times 10^{6}$	32,250	24,500	7,731	4,075
SLURRY SOLIDS CONTENTS WT %		12.0	12.0	12.0	0.0	50	0.0
TOTAL FLOW GPM		8,540	8,540	59.8	49.0	10.8	4.5
pH		6.4	4.87	6.4	6.7	6.7	8.0
TEMPERATURE °F		110	110	110	110	110	60
LIQUID COMPOSITION (MOLALITY)							
SO_2		2.87×10^{-3}	8.34×10^{-3}	2.87×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	—
CO_2		5.84×10^{-3}	4.20×10^{-4}	5.84×10^{-3}	7.12×10^{-3}	7.12×10^{-3}	4.55×10^{-4}
SO_3		5.45×10^{-2}	5.55×10^{-2}	5.45×10^{-2}	5.48×10^{-2}	5.48×10^{-3}	6.25×10^{-4}
CaO		1.25×10^{-2}	1.35×10^{-2}	1.25×10^{-2}	1.21×10^{-2}	1.21×10^{-2}	8.74×10^{-4}
MgO		4.67×10^{-2}	4.67×10^{-2}	4.67×10^{-2}	4.67×10^{-2}	4.67×10^{-2}	3.29×10^{-4}
Na_2O		—	—	—	—	—	—
HCL		7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.06×10^{-4}
TDS, WPPM				7,437	7,375	7,375	156
SOLIDS COMPOSITION WT %							
$[(CaSO_3)\cdot.86\cdot(CaSO_4)\cdot.14]\cdot.5H_2O$		87.11	87.16	87.11		87.21	
$CaSO_4 \cdot 2H_2O$							
$CaCO_3$	95.0	7.38	7.31	7.38		7.38	
$MgCO_3$	0.5						
INERTS	4.5	5.51	5.53	5.53		5.51	

SYSTEM CHARACTERISTICS

LIQUID-TO-GAS RATIO	300 GALLONS/ 10^3 ACF (SAT'D)
HOLD TANK VOLUME	32,000 GALLONS
THICKENER DIAMETER	39 FT.
VACUUM FILTER AREA	43.9 FT.^{2}

DESIGN CONDITIONS

FLUE GAS ANALYSIS AND FLOW

	100	101
ACFM	78,800	78,720
lb MOLES/hr.	4,000	3,992
lbs/hr	112,900	112,300
TEMPERATURE °F	110	110
PRESSURE PSIA	14.16	14.19
COMPOSITION MOLE % COMPONENT		
SO_2	0.68	0.03
SO_3	0.03	0.03
HCL	NIL	NIL
O_2	17.03	16.99
N_2	72.08	72.11
H_2O	8.92	8.97
CO_2	1.26	1.91
TOTAL	100.00	100.00

NOTE: ALL VALUES ARE FOR TOTAL SYSTEM FLOW

MOLYCORP LIMESTONE SCRUBBING SYSTEM

FIGURE 7-3

Figure 19. Molycorp limestone scrubbing system.

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Process Description--

The dual alkali process uses a solution of sodium compounds (i.e., Na_2SO_3, Na_2CO_3, $NaHSO_3$, $NaOH$) to remove SO_2 from flue gases. The reacted solution is then regenerated using a calcium-based alkali, usually lime. Sulfur species precipitate from the solution as a calcium sulfite/sulfate sludge which can be disposed of in a pond or landfill.

The overall process consists of three basic steps: absorption, regeneration, and separation. The principal reactions are described by the following equations:

Absorption

$$2\ NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad (27)$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3 \qquad (28)$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \qquad (29)$$

Regeneration

$$Ca(OH)_2 + 2\ NaHSO_3 \rightarrow Na_2SO_3 + CaSO_3\ \tfrac{1}{2}H_2O\ (s) + 3/2\ H_2O \qquad (30)$$

$$Ca(OH)_2 + Na_2SO_3 + \tfrac{1}{2}H_2O \rightarrow 2\ NaOH + CaSO_3 \cdot \tfrac{1}{2}H_2O\ (s) \qquad (31)$$

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightleftharpoons 2\ NaOH + CaSO_4 \cdot 2H_2O\ (s) \qquad (32)$$

A simplified flow diagram for the dual alkali system is shown in Figure 20. Most of the scrubber effluent is recycled to the scrubber for the absorption step. A slipstream of the recycled slurry is withdrawn and regenerated in a separate tank. Regeneration is generally performed with lime in the United States; however, limestone has been used as a regenerant in Japan.

In the FMC process, the regeneration occurs in a continuous stirred tank reactor at a pH of about 8.5. At this pH, reaction 30 is prevalent. CEA/ADL utilizes a specially designed two-stage reactor system which operates at a pH of 11 to 12.5 such that both reactions 30 and 31 occur.

The regenerated solution is then routed through solid-liquid separation equipment. Solids can be concentrated to approximately 60 percent in a thickener followed by a vacuum filter. The resulting cake is washed to minimize sodium loss with the sludge. The clear overflow from the thickener is pumped back into the scrubber absorption loop.

An additional step is sometimes used between the separation and absorption processes. Normally this step is only required when oxidation is high and the system is operating in a dilute mode as discussed below. A system with oxidation greater than 25 percent is termed a "dilute" system. A softening reagent may be added to prevent sulfate scaling by adding sodium carbonate in a reaction/thickener vessel to precipitate calcium carbonate. This lowers the $CaSO_4$ relative saturation and minimizes possible scale formation (5,12,14).

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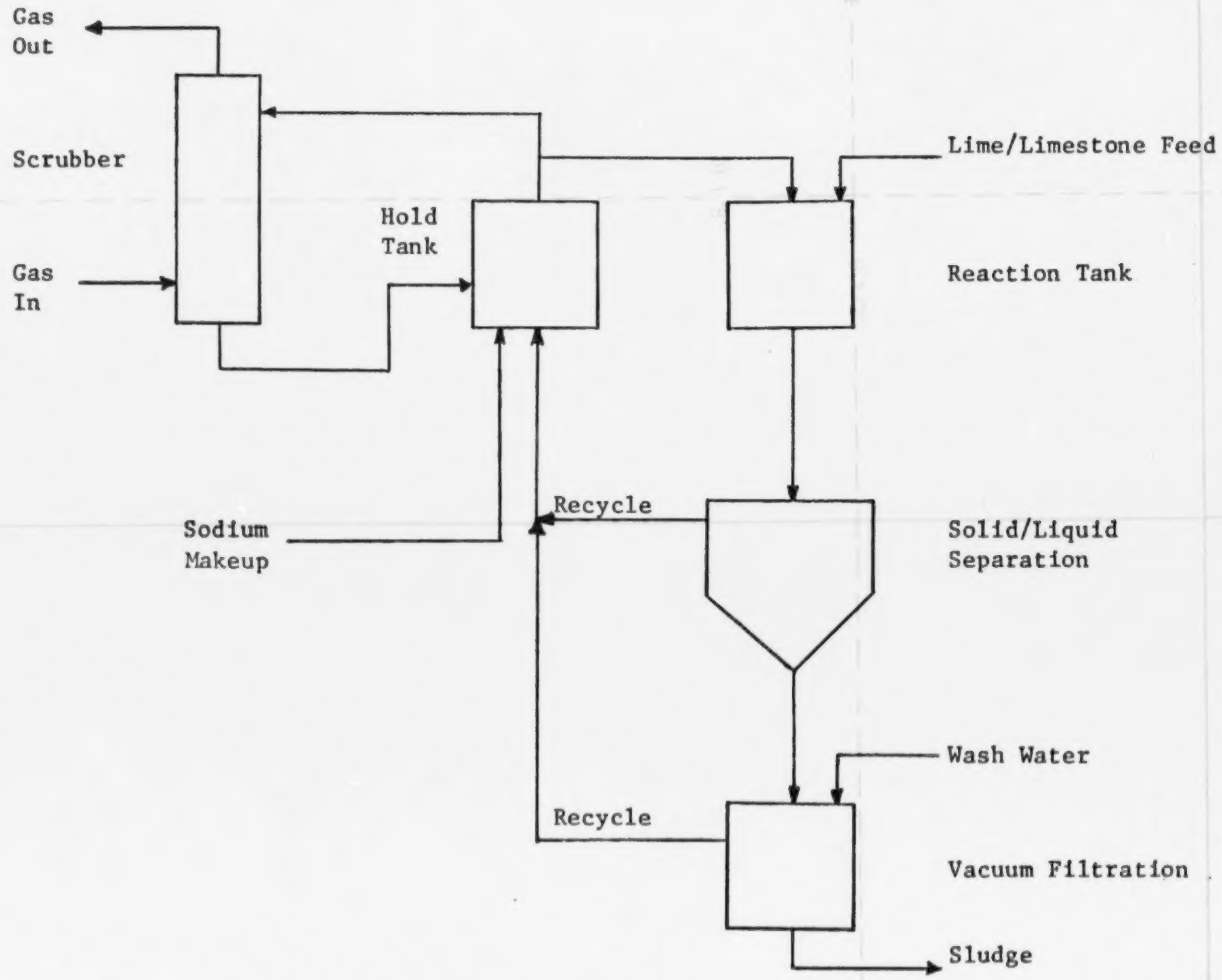

Gas Out
Scrubber
Gas In
Hold Tank
Lime/Limestone Feed
Reaction Tank
Sodium Makeup
Recycle
Solid/Liquid Separation
Wash Water
Recycle
Vacuum Filtration
Sludge

Figure 20. Simplified dual alkali system.

Applicability to Smelter/Roaster Offgases--

The dual alkali process appears capable of handling flue gas with a high SO_2 concentration. The degree of oxidation has a profound effect on the mode of operation of the system however. As long as the oxidation remains below approximately 25 percent, the sulfate will be removed as a coprecipitate with the sulfite. This so-called "concentrated" system can be regenerated with lime or limestone and contains sulfite as the major dissolved sulfur species. In cases where the sulfite oxidation is greater than 25 percent, the sulfate concentration builds up in solution. This increase in sulfate concentration results in a higher concentration of inactive sodium (Na_2SO_4) thereby reducing the active sodium concentration ($NaOH$, Na_2CO_3, $NaHCO_3$, Na_2SO_3, $NaHSO_3$) below .15 M. The liquor is then saturated or supersaturated with calcium sulfate after regeneration.

In the "concentrated" system, sulfite reacts with SO_2 to form bisulfite (Equation 28). The regenerated liquor from the concentrated system can absorb more SO_2 per unit volume. This means lower liquor volumes and L/G's and lower equipment and operating costs.

Sodium losses in the sludge can be reduced in both cases by washing the cake prior to disposal. Washing the sludge cake can cause water balance problems if the system is to run as a closed loop operation. Land requirements for sludge disposal are approximately the same as a limestone system.

Equipment Sizing--

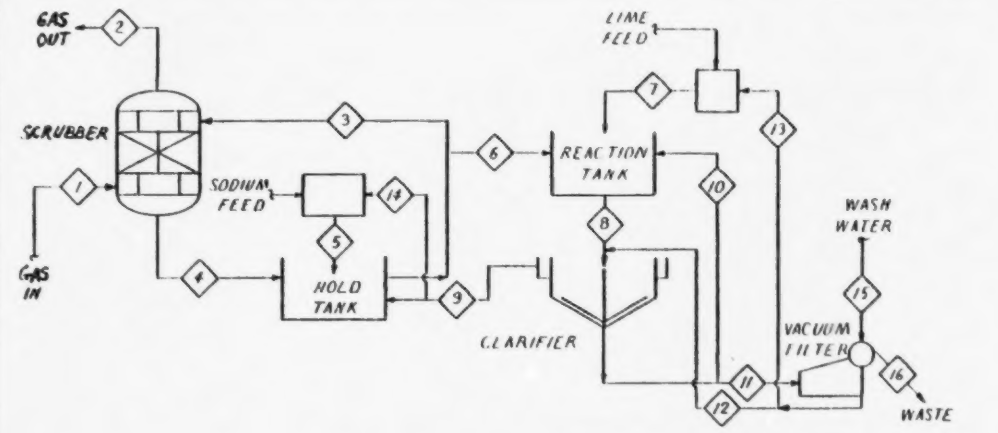
The results of the Radian bench-scale studies with lime indicate that the oxidation may be low enough to run a concentrated system. Hence, coprecipitation of $CaSO_4$ with $CaSO_3$ should provide adequate sulfate removal. This has to be confirmed for the double alkali system through longer-term experiments in a pilot unit before a full-scale system can be designed with confidence.

An estimate of the stream flows and equipment requirements for Molycorp are shown in Figure 21. These are based upon the inlet gas conditions given previously. A lime additive stoichiometry of 1.05 was specified. From Radian computer simulations of the dual alkali system, a pickup of 45 mmoles SO_2 per liter of scrubbing solution is estimated. From this value the liquid-to-gas ratio at Molycorp is 40 gallons per 1000 acf (saturated) is calculated. The design parameters for slurry feed pumps, alkali feed rate, hold tank, reaction tank, clarifier and vacuum filter are shown in Table 6. These values are based on data for existing dual alkali systems.

4.1.3 Magnesia Slurry Scrubbing Process

Currently, Philadelphia Electric Co. has the only operating, full-scale magnesia slurry scrubbing process in the U.S. Salable 98 percent sulfuric acid has been produced during preliminary performance testing; however, the system's cumulative availability during this period was only 32 percent (6).

Philadelphia Electric Co. has also committed to three additional units which are now under construction (Cromby 1 and Eddystone units 1 and 2).(8)


GAS OUT
2
SCRUBBER
1
GAS IN
3
4
SODIUM FEED
5
14
HOLD TANK
6
9
LIME FEED
7
REACTION TANK
8
10
13
CLARIFIER
WASH WATER
15
VACUUM FILTER
11
12
16
WASTE

	FLUE GAS 1	2
ACFM	28,800	28,610
lb/hr	112,860	111,190
lb mole/hr	4,000	3,974
T (°F)	110	110
% SO_2	.68	.034

REACTION TANK = 10,000 GAL.

HOLD TANK = 20,400 GAL.

R = 95%

L/G = 40 GAL/MACF

70-1304-2

STREAM	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
TOTAL FLOW - lb/hr	586,580	588,160	760	105,100	7,000	115,500	103,290	3,400	12,000	3,190	4,900	610	2,090	6,000	
SOLIDS FLOW - lb/hr			150		2,100	4,620		1,020	3,600					3,600	
LIQUIDS FLOW - lb/hr	586,580	588,160	610	105,100	4,900	110,880	103,290	2,380	8,400	3,190	4,900	610	2,090	2,400	
SLURRY WT% SOLIDS			20		30	4		30	30					60	
TOTAL FLOW GPM	1,150	1,153	1	206	12	221	203	6	20	6	10	1	4	8	
DENSITY lb/gal	8.5	8.5	9.6	8.5	10.0	8.7	8.5	10.2	10.2	8.5	8.5	8.5	8.5	12.7	
SOLIDS COMPOSITION WT%															
-$Ca(OH)_2$					95.0	3.5		3.5	3.5					3.5	
-$Na_2CO_3 \cdot H_2O$			100												
-$CaSO_3 \cdot \frac{1}{2}H_2O$						79.0		79.0	79.0					79.0	
-$[(CaSO_3) \cdot 85(CaSO_4) \cdot 15] \cdot \frac{1}{2}H_2O$						14.0		14.0	14.0					14.0	
-INERTS					5.0	3.5		3.5	3.5					3.5	

Figure 21. Molycorp dual alkali process material balance.

TABLE 6. MOLYCORP EQUIPMENT SIZING AND DESIGN PARAMETERS FOR DUAL ALKALI SYSTEM

	Design Parameter (References)	Calculated Size for Molycorp
Slurry feed pumps	45 mmole/ℓ SO_2 pickup	1150 gpm
Alkali feed rate	1.05 stoichiometry, 95% $Ca(OH)_2$ in lime	2100 lbs/hr
Hold tank	15 minute residence time	20400 gallons
Reaction tank	45 minute residence time (LA-324)	10000 gallons
Clarifier	0.4 gpm/ft^2 (EN-269)	27 ft diameter
Vacuum filter	88 $lb/hr\text{-}ft^2$(GL-079)	41 ft^2

The process vendor in each case is United Engineers. Chemico also offers a magnesia slurry process. They demonstrated their system at Boston Electric's Mystic Station.

Process Description--

The magnesia slurry process can be divided into four basic steps: SO_2 absorption, $MgSO_3/MgSO_4$ separation and drying, MgO regeneration, and SO_2 conversion. A simplified schematic of the magnesia slurry FGD system is shown in Figure 22.

An aqueous slurry of magnesium hydroxide and magnesium sulfite (pH 6.5-8.5) is used to absorb SO_2 according to Equations 33 and 34.

$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O \qquad (33)$$

$$MgSO_3 + H_2O + SO_2 \rightarrow Mg(HSO_3)_2 \qquad (34)$$

Sulfite oxidation gives rise to sulfates in the system by the following reaction:

$$MgSO_3 + \tfrac{1}{2}O \rightarrow MgSO_4 \qquad (35)$$

The bisulfite in the spent scrubbing liquor is reacted with magnesium hydroxide which is formed by slaking the fresh and recycle magnesium oxide.

$$Mg(HSO_3)_2 + Mg(OH)_2 + 4H_2O \rightarrow 2(MgSO_3 \cdot 3H_3O) \qquad (36)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (37)$$

Excess $MgSO_3$ is precipitated from the slurry as a solid. Makeup water, recycle MgO, and makeup MgO are added to the recycle slurry to maintain a constant slurry composition (16).

The sulfite and sulfate solids precipitate as hydrated crystals as illustrated in the following equations:

$$MgSO_3 + 6H_2O \rightarrow MgSO_3 \cdot 6H_2O \qquad (38)$$

$$MgSO_3 + 3H_2O \rightarrow MgSO_3 \cdot 3H_2O \qquad (39)$$

$$MgSO_4 + 7H_2O \rightarrow MgSO_4 \cdot 7H_2O \qquad (40)$$

The hydrate form is governed by temperature and solution composition (ionic strength) (15). The hexahydrate is preferred because its large crystals are easily separated.

A portion of the 10-15 weight percent slurry from the main scrubber circulation loop is removed and sent to a thickener. The thickener is an optional piece of equipment that has the potential for increasing the surge capacity in the recovery portion of the plant and also for improved centrifuge operation (16).

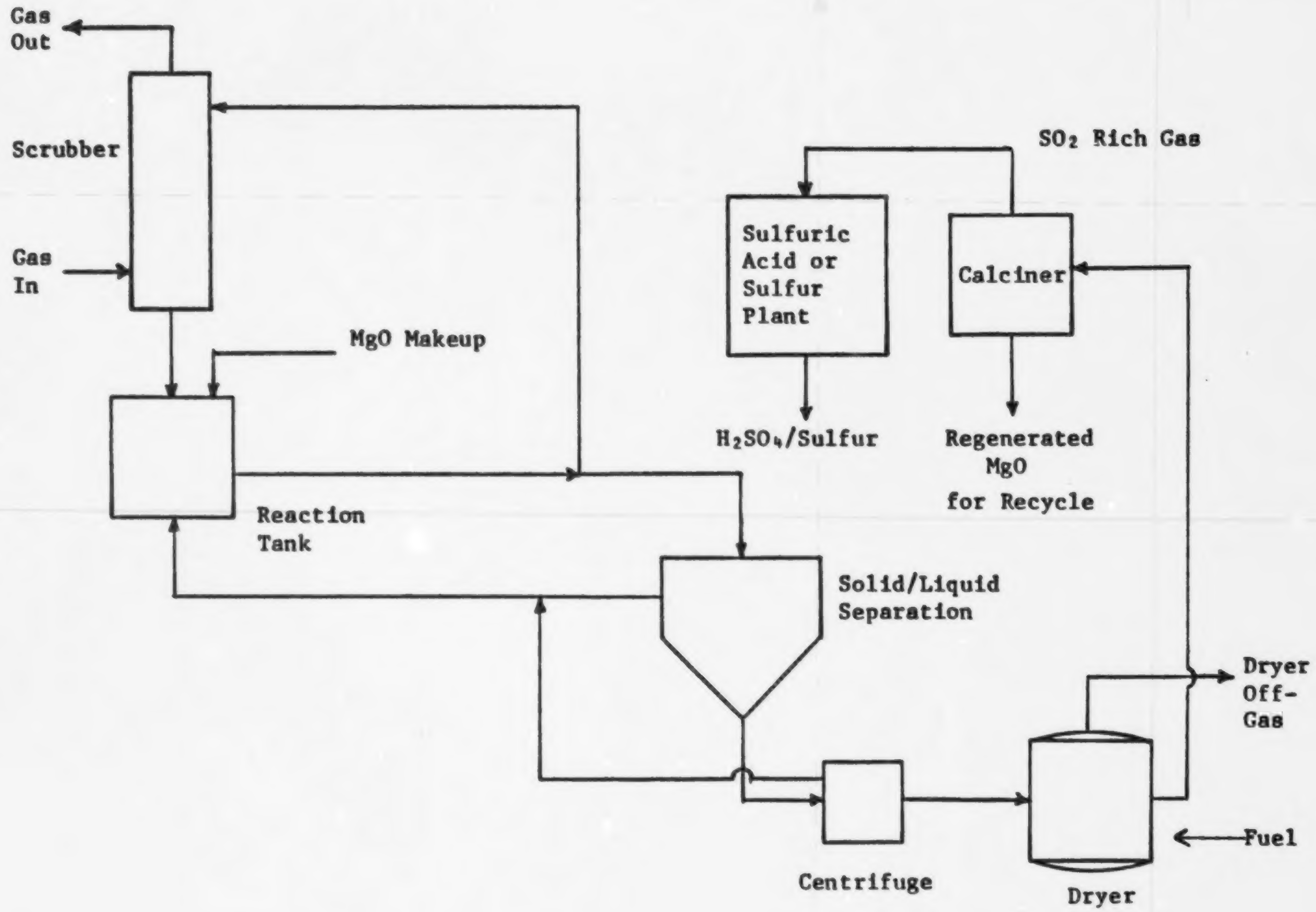

Gas Out
Scrubber
Gas In
MgO Makeup
Reaction Tank
Sulfuric Acid or Sulfur Plant
Calciner
SO₂ Rich Gas
H₂SO₄/Sulfur
Regenerated MgO for Recycle
Solid/Liquid Separation
Dryer Off-Gas
Centrifuge
Dryer
Fuel

Figure 22 - Simplified magnesia slurry system

A stainless steel, solid bowl centrifuge can recover a wet cake of $MgSO_3/MgSO_4$ hydrate crystals. Satisfactory centrifuge operation is necessary so that solids are removed at a sufficient rate to maintain control of recycle solids concentration. Wet crystals are discharged from the centrifuge through a vertical chute into a screw feeder which provides a seal and a continuous flow of wet solids into a rotary or fluid-bed dryer. The rotary kiln type dryer has been used in the three U.S. magnesia scrubbing units. The dried $MgSO_3/MgSO_4$ is discharged from the dryer and sent to the MgO regeneration and SO_2 recovery section.

Dried $MgSO_3/MgSO_4$ solids are heated in a rotary kiln or fluidized-bed reactor until decomposed. The main decomposition reaction is shown in Equation 41. The $MgSO_4$ is also reduced in the calciner using carbon as a reducing agent (Equation 42).

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (41)$$

$$MgSO_4 + \tfrac{1}{2}C \rightarrow MgO + SO_2 + \tfrac{1}{2}CO_2 \qquad (42)$$

Two installations have used a rotary kiln to regenerate the MgO. High dust losses in the rotary kiln require the use of a hot cyclone and venturi scrubber to recover all of the MgO. If a fluidized-bed reactor was used, most of the MgO formed would go overhead with the SO_2 and combustion gases and separation equipment would also be required.

The optimum calcining temperature in the reactor is set by the minimum temperature required to decompose all of the $MgSO_3/MgSO_4$ solids without "dead burning" the MgO. "Dead burned" MgO is chemically unreactive and not effective for further SO_2 removal. Operating temperatures in the 1500°F range have been used for rotary calciners in this service (15).

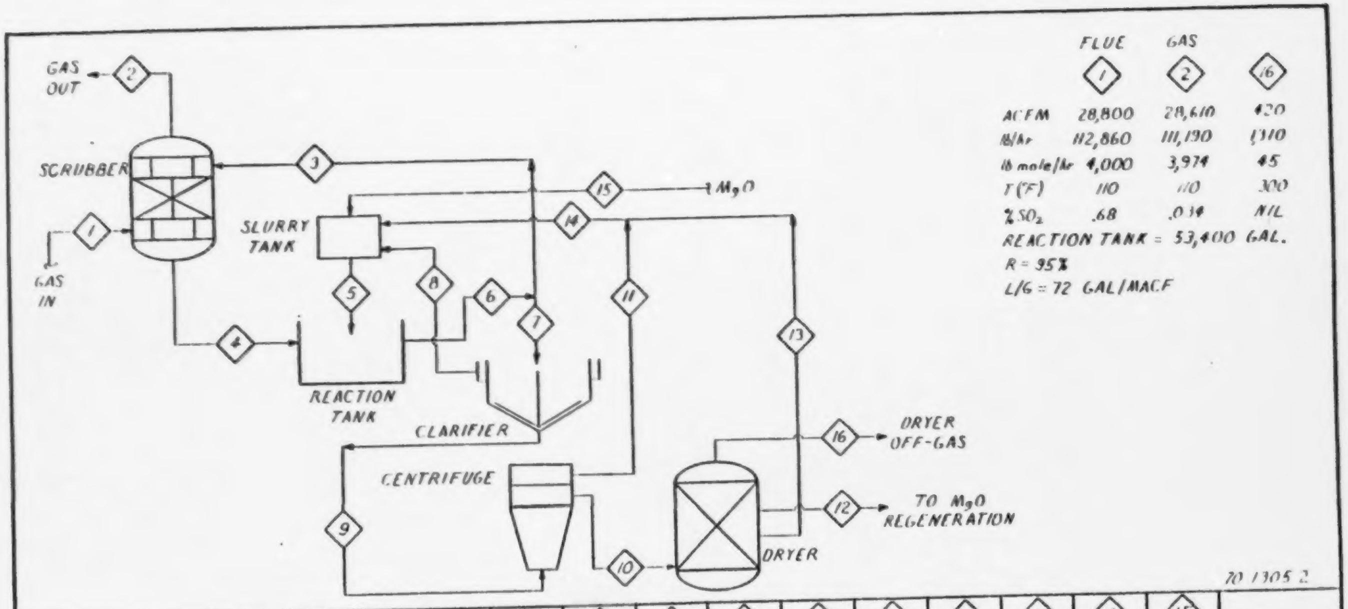
The SO_2 rich stream from the calciner can be used to produce elemental sulfur or sulfuric acid. These options are discussed more fully in the next section on smelter/roaster applicability.

Applicability to Smelter/Roaster Offgases--

The magnesia slurry process appears capable of handling the high SO_2 concentrations in the smelter gas. High removals can be attained with relatively low L/G's. To date no problems have been encountered with oxidation; $MgSO_4$ is reduced by coke in the calciner.

The major concern for smaller installations is the conversion of the calciner gas SO_2 to useful chemicals and the marketing of these products. Two possible products are sulfuric acid or complete reduction to elemental sulfur.

Because the cost of reducing gas required to produce sulfur is relatively high, the sulfur alternative is probably eoncomically prohibitive. Sulfuric acid production may be feasible if the unit is located



GAS OUT
2
SCRUBBER
1
GAS IN
3
4
SLURRY TANK
5
8
6
7
15
Mg O
14
11
13
REACTION TANK
CLARIFIER
CENTRIFUGE
9
10
DRYER
16
DRYER OFF-GAS
12
TO MgO REGENERATION
70 1305 2

	FLUE ◇1	GAS ◇2	◇16
ACFM	28,800	28,610	420
lb/hr	112,860	111,190	1,310
lb mole/hr	4,000	3,974	45
T (°F)	110	110	300
% SO_2	.68	.034	NIL

REACTION TANK = 53,400 GAL.
R = 95%
L/G = 72 GAL/MACF

STREAM	◇3	◇4	◇5	◇6	◇7	◇8	◇9	◇10	◇11	◇12	◇13	◇14	◇15	
TOTAL FLOW - lb/hr	1,179,900	1,181,560	35,380	1,216,470	36,570	18,270	18,300	8,450	9,850	2,700	5,750	15,600	1,510	
SOLIDS FLOW - lb/hr	176,990	176,990	1,510	182,470	5,490		5,490	5,490		2,700			1,510	
LIQUIDS FLOW - lb/hr	1,002,910	1,004,570	33,870	1,034,000	31,080	18,270	12,810	2,960	9,850		5,750	15,600		
SLURRY WT.% - SOLIDS	15	15	4	15	15		30	65						
TOTAL FLOW - GPM	2,070	2,073	66	2,134	64	35	30	12	19		11	30		
DENSITY - lb/gal	9.5	9.5	8.9	9.5	9.5	8.7	10.2	12.0	8.7		8.7	8.7		
SOLIDS COMPOSITION WT%														
- $MgSO_3 \cdot 6H_2O$	100	100		100	100		100	100					100	
- $Mg(OH)_2$														
- $MgSO_3$										100				

Figure 23. Molycorp magnesia slurry process material balance.

in the proximity of a potential market so that transportation costs can be minimized. The best alternative may be to locate the regeneration facility off-site. Transportation would then involve only the shipping of the magnesia solids. The economic implications of each of these by-product routes must be carefully examined before final selection.

A final possibility is the direct production of elemental sulfur in the calciner. While a study has shown this to be thermodynamically possible, to date it has not been demonstrated.

Equipment Sizing--

A flow diagram and stream flow rates for a conceptual magnesia slurry scrubbing system at Molycorp are shown in Figure 23. Regeneration is assumed to be off-site; however, the $MgSO_3/MgSO_4$ solids are assumed to be dried on-site to minimize magnesium loss, water makeup, and shipping costs. The same design basis as used in the dual alkali system (Section 4.1.4) is used in the magnesia slurry design.

From computer simulations of MgO systems, a pickup of 25 millimoles of SO_2 per liter of scrubbing slurry should provide a resonable estimate for the liquid-to-gas ratio. Using this pickup rate, the L/G is estimated at 72 gallons per 10^3 acf (saturated).

The magnesium system at Molycorp will require a 53,400 gallon reaction tank (25 minute residence time). The clarifier is estimated to be similar in size to the one in the dual alkali design. The centrifuge and drier are designed to handle approximately 1,500 lb/hr of dry solids.

In addition to the magnesium makeup in the operating scrubber, the system will require magnesium to makeup solids in transit to the off-site acid plant if the off-site by-product alternative were selected. The reserve for the transit magnesium is approximately equal to one week of magnesium oxide makeup.

4.1.4 Wellman-Lord Process

The Wellman-Lord sulfite scrubbing process marketed by Davy McKee is based on the ability of sodium sulfite solution to absorb SO_2, thus forming a solution of sodium bisulfite which can be thermally regenerated. A commercial-scale unit was successfully operated at Northern Indiana Public Service Company's (NIPSCO) Mitchell Station. A concentrated stream of SO_2 is produced which can be processed to elemental sulfur, sulfuric acid, or liquid SO_2. A by-product purge of sodium sulfate is produced as the result of sulfite oxidation. Antioxidants have been used to reduce the sulfate purge rate, but have been found to be uneconomical.

Process Description--

A simplified process flow sheet appears in Figure 24. The Wellman-Lord Process consists of five basic processing steps: gas pretreatment, absorption, purge treatment, regeneration, and SO_2 conversion.

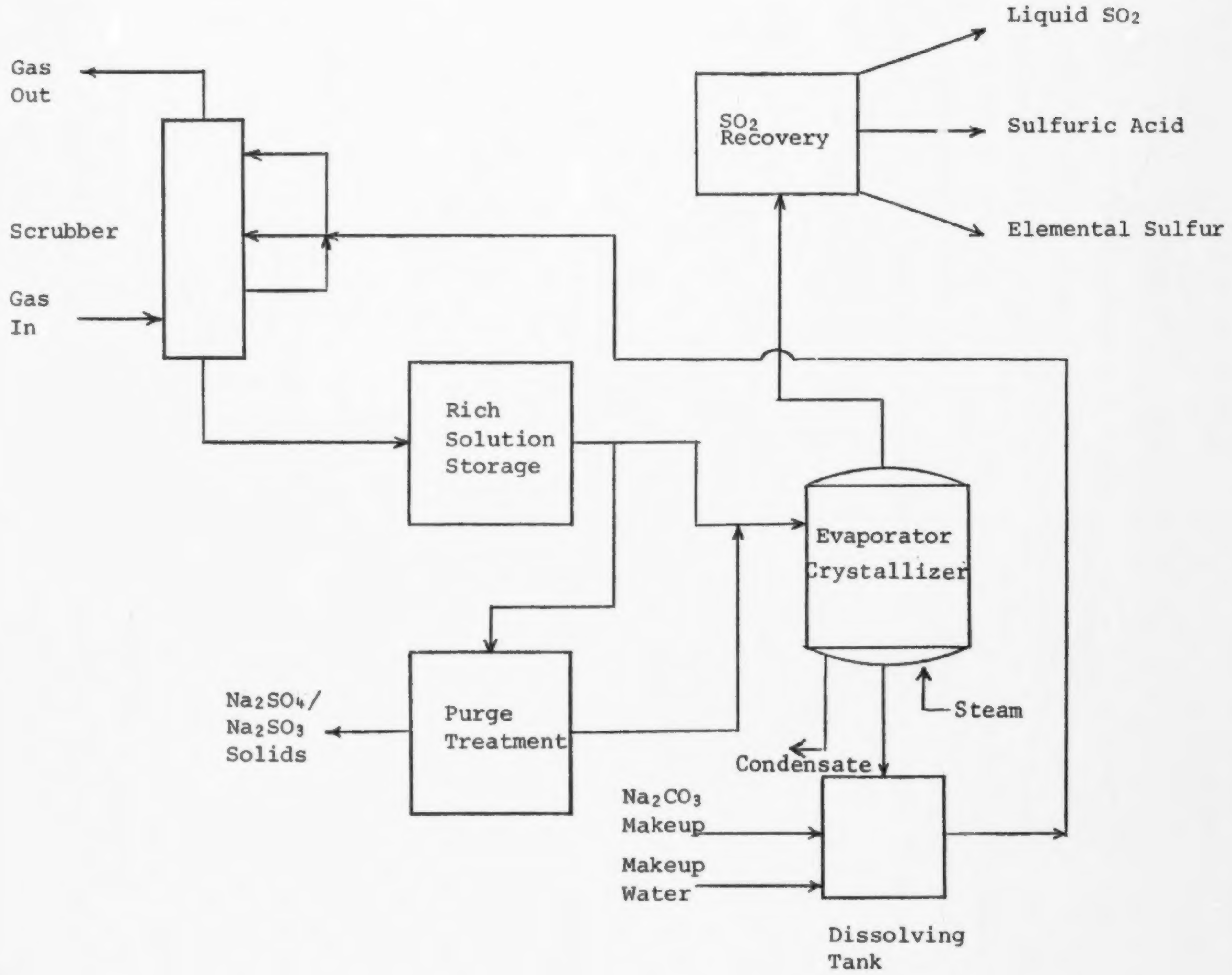

Gas Out
Scrubber
Gas In
Rich Solution Storage
Purge Treatment
Na_2SO_4/ Na_2SO_3 Solids
SO_2 Recovery
Liquid SO_2
Sulfuric Acid
Elemental Sulfur
Evaporator Crystallizer
Steam
Condensate
Na_2CO_3 Makeup
Makeup Water
Dissolving Tank

Figure 24. Simplified Wellman-Lord system.

No unusual or unique equipment is used in any of these areas with the possible exception of SO_2 conversion step which is licensed technology. The gas pretreatment section is essentially the same as found in most aqueous scrubbing systems.

Humidified gas from the prescrubber is passed through the absorption tower where the SO_2 level is reduced by over 90 percent. The cleaned gas may be reheated by several methods prior to exhausting the gas but use of steam allows coal to be used indirectly rather than direct combustion of premium fuels such as oil or natural gas.

Absorption of SO_2 proceeds according to Equation 43.

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \qquad (43)$$

Makeup sodium carbonate also reacts with SO_2 in the absorber to form sodium sulfite by Equation 44.

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \qquad (44)$$

A very important side reaction which will be discussed later is oxidation of the sulfite to sulfate.

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \qquad (45)$$

Some sodium sulfate is also formed by absorption of SO_3 from the flue gas:

$$2Na_2SO_3 + SO_3 + H_2O \rightarrow 2NaHSO_3 + Na_2SO_4 \qquad (46)$$

Davy McKee offers two types of absorption units; a packed tower for small volume applications and a valve tray tower for large volume applications. The valve tray unit is generally built in a square configuration and includes three to five trays depending on the inlet SO_2 concentration and the degree of desulfurization. Because the concentrated sodium sulfite solution has a large capacity to absorb SO_2, the feed liquor flow is fairly small and recirculation is practiced on each stage to maintain good hydraulic characteristics over the trays. With the recirculation, the L/G ratio is kept at about 40-45 gal/mscf. Superficial gas velocity in the absorber is about 10 feet per second (15).

About 20 percent of the absorber product liquor is drawn off to the purge treatment area for separation of sodium sulfate. Feed liquor is cooled by heat exchange with treated liquid. In a chiller-crystallizer the purge is further cooled to about 32°F and a mixture of sodium sulfate and sulfite is crystallized out. The slurry is put through a centrifuge to produce a 40 percent solids cake and the cake is dried using steam. A small liquid purge stream is also drawn off the evaporators in the regeneration section and added to the cake to remove some of the thiosulfate formed in the system. The crystalline product is a mixture of anhydrous sodium sulfate (70 percent) and sodium sulfite (30 percent), plus small amounts of thiosulfates and pyrosulfites. The vent gases from the dryer are scrubbed to remove dust and

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recycled to the main flue gas stream. The centrate is heated by passing through the feed cooler and is returned to the product liquor stream entering the evaporator loop. Refrigeration for the chiller-crystallizer is provided by an ethylene glycol system (15).

The regeneration section consists of a set of double effect, forced circulation evaporators, condensers, a condensate stripper, and a dissolving tank. Regeneration of sodium sulfite is performed by simply reversing the absorption reaction through addition of heat as shown in reaction 47.

$$2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + SO_2 \qquad (47)$$

However, higher temperatures also increase the formation of thiosulfate by the following disproportionation reactions.

$$6NaHSO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + 2SO_2 + 3H_2O \qquad (48)$$

$$2NaHSO_3 + 2Na_2SO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + H_2O \qquad (49)$$

The combined stream of absorber product liquor and purge centrate is split between the two evaporator effects, each of which operates under a vacuum, with 55 percent going to the first effect and 45 percent going to the second effect. The first effect operates at 200°F and is heated with low pressure steam by way of an external shell and tube exchanger. The SO_2 and water vapor driven off in the overhead from the first effect are used to heat the second effect which operates at about 170°F. In each effect the undissolved solids content of the recirculated liquor is about 45 percent, primarily sodium sulfite. Operating at such a high solids concentration eliminates the need to centrifuge the product stream going to the dissolving tank. The regeneration reaction is limited by the equilibrium concentration of sulfite ion in solution. Fortunately, since sodium sulfite is less soluble than sodium bisulfite, it is continuously removed from solution by crystallization driving the reaction forward.

The SO_2 and water vapor from the evaporators is subjected to partial condensation to remove most of the water and concentrate the SO_2. The SO_2 is then compressed and sent to the SO_2 conversion section (15).

One of three product options may be selected for conversion of gaseous SO_2 to useful chemicals: (1) liquid SO_2, (2) sulfuric acid, or (3) elemental sulfur. These options will be discussed in more detail in the following smelter/roaster applicability section.

Applicability to Smelter/Roaster Offgases--

The Wellman-Lord Process appears capable of handling the high SO_2 concentration in the smelter gas. Oxidation may prove a problem due to the presence of trace elements which enhance oxidation. This could increase the purge rate required to prevent the buildup of sodium sulfate in the system. Also, sodium losses will increase with increased purge rate resulting in higher sodium makeup requirements.

TYPING GUIDE SHEET

A primary concern with the Wellman-Lord Process is how to convert the gaseous SO_2 from the evaporator/crystallizer to salable chemicals. The three possible products are:

- compression and liquefication for sale as liquid SO_2,
- catalytic oxidation to produce sulfuric acid, and
- reduction to elemental sulfur.

The amount of SO_2 which could be recovered for sale can be estimated from the evaporator offgas assuming an overall oxidation of 15 percent. The SO_2 from the offgas is calculated to be 15.7 tons/day. Assuming all the gaseous SO_2 can be converted, the sulfuric acid would be 24 tons/day. If all the SO_2 were reduced to elemental sulfur the production would be 7.8 tons/day.

Each of these choices has drawbacks. All require the location of a potential buyer within a reasonable distance since transportation costs can be significant. In addition, special storage facilities are required for the liquid SO_2 or sulfuric acid products. Elemental sulfur does not present as large a storage problem, however, it is the most expensive alternative.

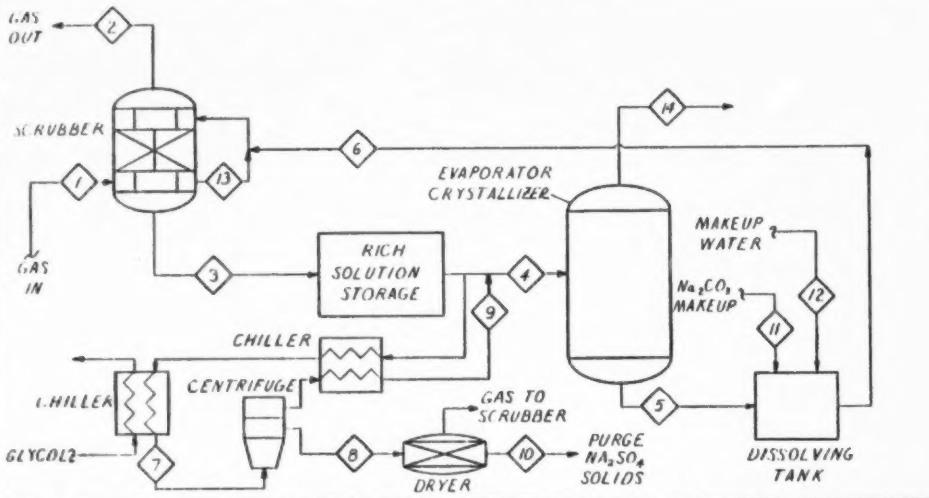
Equipment Sizing--

A simplified process flow scheme and stream flow rates for a Molycorp Wellman-Lord system are shown in Figure 25. Stream flow estimates and equipment sizing are based on the conditions set forth previously. Based on the similarity between the dual alkali and Wellman-Lord systems, the liquid-to-gas ratios are assumed to be approximately the same. The liquid feed to the scrubber loop is small due to recirculation of the scrubbing liquor in the scrubber.

Sodium must be added to the system due to the loss in the purge stream. Assuming an oxidation of 15 percent, the Na_2SO_4 purge rate can be estimated at 550 lbs per hour. Assuming the purge solids are 70 percent Na_2SO_4 and 30 percent Na_2SO_3, the total purge rate is 790 lb/hr (15). The sodium carbonate makeup rate is therefore 600 lb/hr.

Since no solids precipitation occurs in either the rich solution storage tank or the dissolving tank, the residence time required is fairly short. Based upon a 15 minute residence time, the tank requirements are 800 gallons for the rich solution storage and 750 gallons for the dissolving tank.

The evaporator/crystallizer is designed to concentrate a 49 gpm liquid stream to approximately 45 percent solids. The centrifuge and dryer in the purge treatment section are required to handle approximately 790 lbs/hr of dry solids.


GAS OUT
2
SCRUBBER
1
13
6
14
GAS IN
3
RICH SOLUTION STORAGE
4
9
EVAPORATOR CRYSTALLIZER
MAKEUP WATER
Na_2CO_3 MAKEUP
11
12
CHILLER
CHILLER
CENTRIFUGE
GLYCOL
7
GAS TO SCRUBBER
8
DRYER
10
PURGE NA_2SO_4 SOLIDS
5
DISSOLVING TANK

	FLUE	GAS	
	1	2	14
ACFM	28,800	28,610	186
lb/hr	112,860	111,190	1,410
lb mole/hr	4,000	3,974	24
T (°F)	110	110	170
% SO_2	.68	.034	85.0

RICH SOL. TANK = 800 GAL.
DISSOLVING TANK = 750 GAL.

70-1303-2

STREAM	3	4	5	6	7	8	9	10	11	12	13	◇	◇	◇	◇	◇
TOTAL FLOW-lbs/hr	27,760	25,780	24,370	26,100	5,840	1,980	3,860	790	600	1,130	571,280					
SOLIDS FLOW-lbs/hr			10,970		790	790		790	600							
LIQUID FLOW-lbs/hr	27,760	25,780	13,400	26,100	5,050	1,090	3,860			1,130	571,280					
SLURRY WT% SOLIDS			45		14	40										
TOTAL FLOW-GPM	53	49	34	50	10	3	7			2	1,034					
DENSITY-lbs/gal	8.7	8.7	12.0	8.7	9.5	11.5	8.7			8.7	8.7					
SOLIDS COMPOSITION WT.%																
Na_2CO_3									100							
Na_2SO_4					70	70		70								
Na_2SO_3					30	30		30								

Figure 25. Molycorp Wellman-Lord process material balance.

4.1.5 Comparison of Capital and Operating Costs for Alternate FGD System

In this section, equipment and cost estimates for the dual alkali, magnesia slurry, and Wellman-Lord processes are compared to the lime/limestone process. These costs are for both capital and operating expenses. The costs come from data in literature (primarily TVA and Radian studies) and information from vendors.

Table 7 shows the relative equipment requirements for each of the processes for which a conceptual design was performed. These are merely estimates and should be used only for comparison purposes.

TABLE 7 EQUIPMENT REQUIREMENTS FOR FGD SYSTEMS
Basis: 10×10^6 lb Mo/yr

	Lime/ Limestone	Dual Alkali	MgO	Wellman-Lord
Clarifier	39 ft	27 ft	14 ft	None
Tanks	57,600 gal	10,000 gal 20,400 gal	53,400 gal	800 gal 750 gal
Vacuum Filter	44 ft^2	41 ft^2	None	None
Centrifuge	No	No	Yes	Yes
Dryer	No	No	Yes	Yes
Other	-	-	-	Evaporator-Crystallizer
L/G (gal/1000 acf)	300	40	72	40

The results of the more detailed design and costing done for a lime/limestone system are used as a comparison standard for the other FGD system evaluated. Since there are more lime/limestone systems currently in operation than any other FGD process, cost information for a variety of design bases is readily available. Since detailed designs are not performed for the remaining systems, utility industry data will be used to compare the system costs. This comparison is qualitative and intended only to show relative costs for a utility application.

The high SO_2 concentrations at Molycorp will tend to increase capital expenses due to relatively larger equipment requirements than for a similar gas flow from a coal-fired boiler. However, scrubber size, duct work and reheat requirements will be similar in cost to that for boiler flue gas are based primarily on total gas flow rate and not SO_2 concentration. Equipment based upon liquid or slurry rates (i.e., tanks, clarifier, dryers, etc.) and solids handling (i.e., limestone feed, sodium makeup, sludge disposal, etc.) will be higher in cost since higher relative flow rates are required to achieve the same SO_2 removals from more concentrated smelter SO_2 streams.

Operating costs will also increase due to higher pumping rates and greater pressure drops across the scrubber. This is most evident in the lime/limestone system which has the highest L/G requirement. The high L/G should tend to minimize the operating cost difference between the lime/limestone system and dual alkali which uses the more expensive sodium carbonate as the alkali reagent. Indirect charges also increase the operating cost since a substantial portion of operating costs is based upon the total capital investment.

From utility experience, regenerable systems (i.e., magnesia slurry and Wellman-Lord) are more capital intensive than the throwaway processes (i.e., lime/limestone and dual alkali). Added costs for regeneration equipment are significant. Operating costs may also be high due to higher energy requirements, reductant costs, and capital charges. These operating costs may be partially offset with revenues from the sale of by-product H_2SO_4 or elemental sulfur. Because the regenerable processes can reuse their sorbent material, they will have lower raw material makeup costs than the nonregenerable processes.

Table 8 shows the relative capital and operating costs for a limestone, dual alkali, magnesia slurry, and Wellman-Lord process on a 500 MW coal-fired boiler. This is an average size new utility-sized operation. Although these systems are an order-of-magnitude larger than the conceptual system at Molycorp, the relative costs should give some limited insight to the possible relative costs for the smaller systems.

TABLE 8. COST ESTIMATES FOR CONCEPTUAL DESIGN PROCESSES (Mid-1979 $)

Process	Capital Investment (dollars)	Operating Cost ($ Per Ton S Removal)
Limestone[1]	36,300,000	310
Dual Alkali[1]	32,400,000	335
Magnesia Slurry[2]	38,100,000	370[4]
Wellman-Lord[3]	44,000,000	470[4]

Basis: 500 megawatt (new) coal-fired boiler
3.5% S coal
90% SO_2 removal

[1] On-site solids disposal

[2] Includes cost of acid plant producing 98% sulfuric acid

[3] Includes cost of sulfur production plant

[4] Excludes sulfur by-product credit, a credit is taken equal to zero from McGlammery, et al, Detailed Cost Estimates from Advanced Effluent Desulfurization Processes; EPA600/2-79-006; Jan. 1979.

4.1.6 Other Potential FGD Systems

There are several additional FGD processes which offer potential for control of SO_2 in smelter offgases. However, many are only developed to bench- or pilot-scale operations. Other potential processes have been demonstrated on full-scale operations but have not been extensively used due to reasons of inadequate or unavailable supplies of raw materials or certain processing limitations. A few of these potential processes are discussed in the next sections.

4.1.6.1 Sulf-X Process

The Sulf-X process simultaneously removes SO_2 and NO_x by scrubbing with ferrous sulfide. Due to the early development status of the process, an overall process design for a large-scale plant has not yet been finalized. The system has been demonstrated at the bench-scale and at a 1 MW plant testing the absorption section. The following represents engineering judgment and developer claims as to actual process configuration and performance.

Flue gas is contacted with a ferrous sulfide-water slurry in a venturi quench vessel to cool the flue gas to the adiabatic saturation temperature. The gas is then contacted with a slurry of FeS in either a venturi, packed tower or tray tower for SO_2 and NO_x removal. The following overall reactions have been reported by the process developer:

$$5FeS + SO_2 + 2H_2O \rightarrow 3FeS_2 + 2Fe(OH)_2 \tag{50}$$

$$4FeS + 2NO + 2H_2O \rightarrow N_2 + 2FeS_2 + 2Fe(OH)_2 \tag{51}$$

$$8FeS + 2NO_2 \rightarrow N_2 + 4FeO + 4FeS_2 \tag{52}$$

It should be emphasized that these reactions are overall reactions and do not include a number of intermediate reactions that the process developer reports are proceeding in the system. At pH of about 5.5 the following secondary reactions become important:

$$3FeS + 6SO_2 + 4H_2O \rightarrow 2FeS_2 + 4H_2SO_4 \tag{53}$$

$$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O \tag{54}$$

$$2FeSO_4 + H_2SO_4 + NO \rightarrow Fe_2(SO_4)_3 + H_2O + \tfrac{1}{2}N_2 \tag{55}$$

It is anticipated that the scrubber pH would be controlled at 5.5 by varying scrubber liquor feed rates. The scrubbed gas is then reheated and routed to the stack. Although the spent sorbent could be disposed of as landfill in some specific situations where large quantities of FeS are readily available, the spent absorbent can be regenerated. The spent absorbent is taken to a thickener so that fly ash is removed, filtered and disposed of. Some FeS would also be lost with this stream.

The thickened slurry is sent to a filtration or centrifugation unit and then to a regeneration kiln. In the regeneration kiln, the iron sulfide is regenerated with carbon (such as coal fines) by the following representative reactions:

$$2Fe(OH)_2 \xrightarrow{\Delta} 2FeO + 2H_2O \qquad (56)$$

$$3FeS_2 + 2FeO + C \rightarrow 5FeS + CO_2 + S^0 \qquad (57)$$

The resulting dry FeS is then reslurried and returned to the absorber section. Offgas from the regeneration kiln is routed to a cyclone for particulate removal and to a condenser for sulfur condensation. Offgases are then routed to the regeneration kiln firebox and finally to the quench vessel for feed to the absorption system.

A flow diagram for the process as presented is found in Figure 26. Recent tests indicate a crusher is not needed prior to reslurrying but this point has not yet been proven conclusively. This does not represent the only configuration for the process but does represent a flow scheme that has been proposed by the process developer.

This process has been operated to date only to verify basic process chemistry and assumptions and has not been operated as an integrated unit. Its ability to handle high SO_2 concentrations has not been proven. Oxidation does not appear to be a problem; however, trace elements and organics from a smelter/roaster operation may result in a low quality sulfur byproduct due to contamination (18).

A once-through type process using mine wastes appears to be more economically attractive to Molycorp. Large quantities of FeS are available in the mine waste products; however, the purity of the waste stream may lower its reactivity. Tests should be run using the waste liquor to determine its SO_2 absorption ability prior to actual pitot testing on a smelter offgas.

4.1.6.2 Endako Process--

Endako Mines currently uses a three-stage water scrubbing system to remove SO_2 from their molybdenum roaster offgases. This system is designed to remove 80 percent of the SO_2 in a 40,000 acfm flue gas stream (1.0-1.2 percent SO_2).

A simplified flow diagram of the Endako process is shown in Figure 27. Recycle tailings water is used to cool the gas in the first two stages and absorb the SO_2 in the third stage. The SO_2 scrubber is a packed tower absorber. The primary cooling stage reduces the gas temperature from 450°F to 100°F. The temperature is further reduced in a secondary cooler to approximately 60°F prior to the absorber.

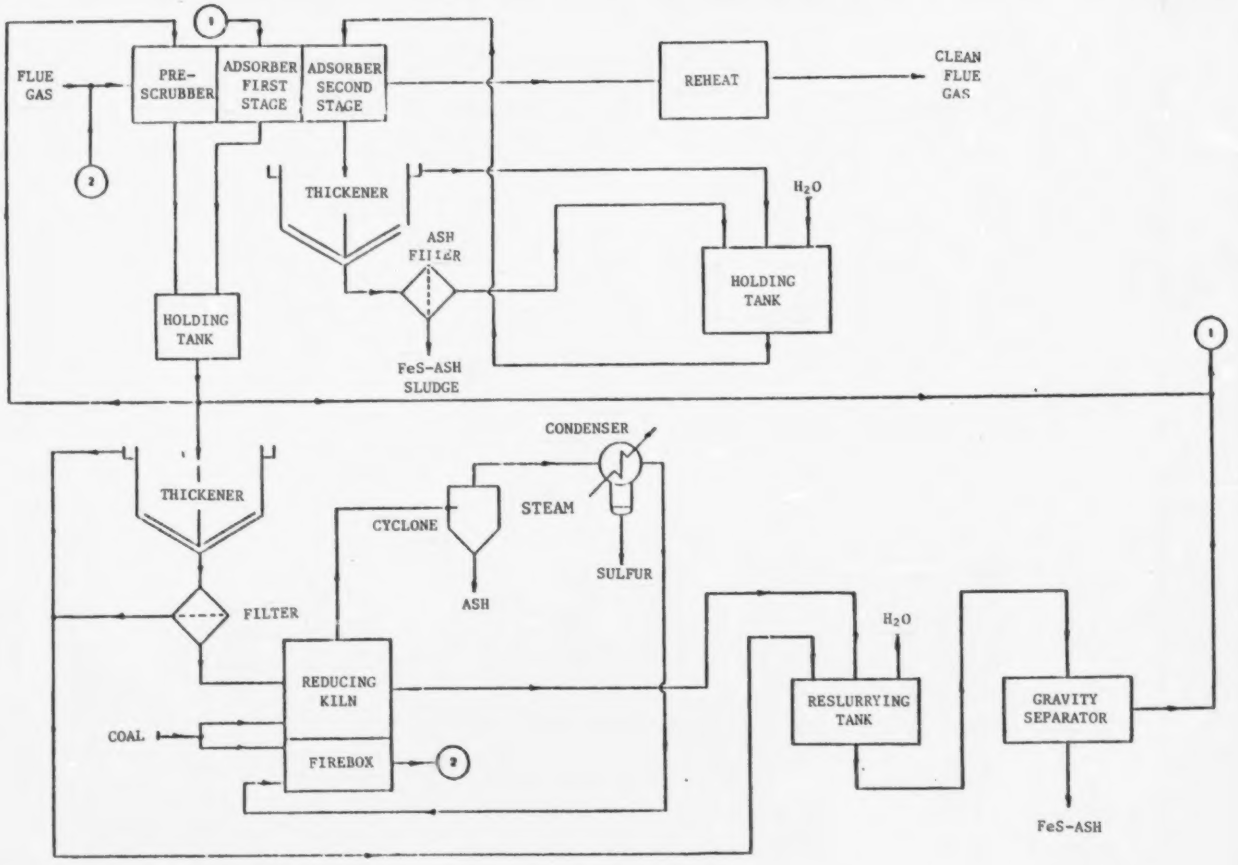

FLUE GAS
PRE-SCRUBBER
ADSORBER FIRST STAGE
ADSORBER SECOND STAGE
REHEAT
CLEAN FLUE GAS
①
②
THICKENER
ASH FILTER
H_2O
HOLDING TANK
HOLDING TANK
FeS-ASH SLUDGE
①
CONDENSER
THICKENER
CYCLONE
STEAM
SULFUR
ASH
FILTER
H_2O
REDUCING KILN
COAL
FIREBOX
②
RESLURRYING TANK
GRAVITY SEPARATOR
FeS-ASH

Figure 26. Simplified flow diagram for Sulf-X process.

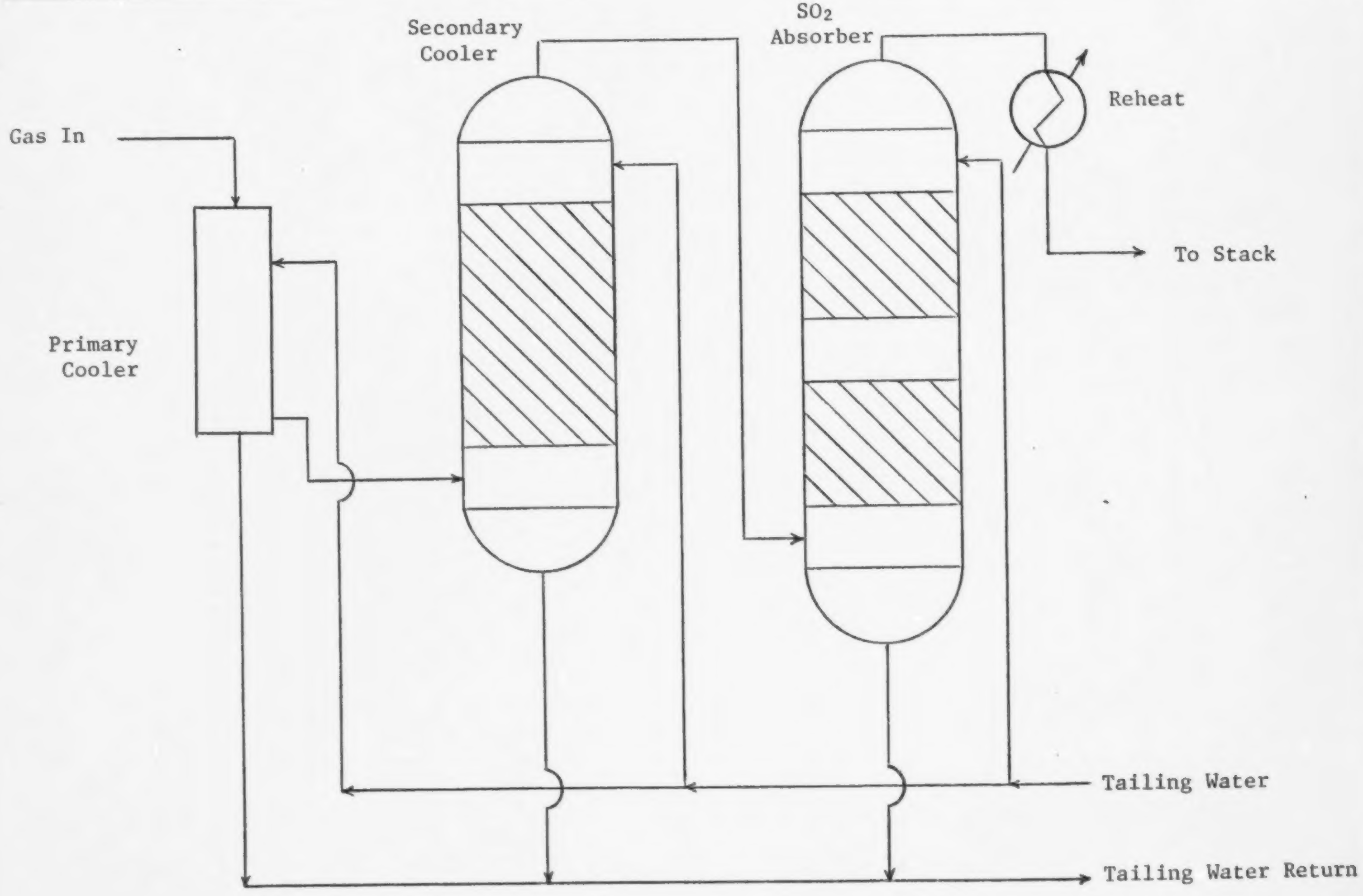

Secondary
Cooler
SO_2
Absorber
Gas In
Reheat
To Stack
Primary
Cooler
Tailing Water
Tailing Water Return

Figure 27. Simplified flow diagram for Endako SO_2 scrubbing process.

Effluent from the process is sent to the mill tailings pond where the dissolved SO_2 reacts with calcite ($CaCO_3$) in the mill tailings to produce a neutral salt and carbon dioxide. Calcite available in the ore is an order of magnitude greater than that required to neutralize the absorbed SO_2.

Two potential problem areas with this process are gas reheat and scrubbing water temperature variations. Due to the low exit gas temperature (60°F), a significant amount of reheat is required to disperse the scrubbed gas. Limestone system exit gas temperatures are typically 130°F. Thus, the reheat energy requirements for the Endako process will be greater.

Variations in the tailing water temperature will greatly affect the removal efficiency for this process. Endako Mines report a substantial variation in the removal of SO_2 under summer and winter conditions. This is probably the biggest problem which this process presents with reference to Molycorp.

The Endako SO_2 removal process is certainly a very inexpensive process compared to other FGD control methods. Whether it can achieve the higher removal (up to 95 percent) required at Molycorp under their climatic conditions is not known (9).

4.1.6.3 Chiyoda Thoroughbred 121 Process--

The Chiyoda Thoroughbred 121 (CT-121) process is a second generation process that Chiyoda expects to replace their CT-101 process. Many of the CT-101 process steps are combined in the CT-121 process which utilizes a single reactor system to absorb and oxidize the SO_2, and neutralize the resulting acids with limestone. The overall reaction in the system is given by:

$$SO_2 + CaCO_3 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \tag{58}$$

A simplified flow diagram of the CT-121 process is shown in Figure 28. Hot flue gases are cooled in a water scrubber and sparged into a tank containing water, limestone and gypsum. Air is also sparged through the solution to oxidize calcium sulfite to calcium sulfate. The flue gas is routed through mist eliminators, reheated and discharged through the stack. Gypsum is continually removed from the bottom of the scrubber as a slurry and pumped to a pond. The resulting gypsum stream can be landfilled or sold for wallboard production.

The CT-121 process appears to be capable of handling the high SO_2 concentrations in smelter/roaster offgases. Natural oxidation of sulfite to sulfate which could limit the applicability of some FGD processes to smelter operations is not a problem with this process. Any natural oxidation will in fact reduce the air required to force oxidize the calcium sulfite to the desired calcium sulfate product.

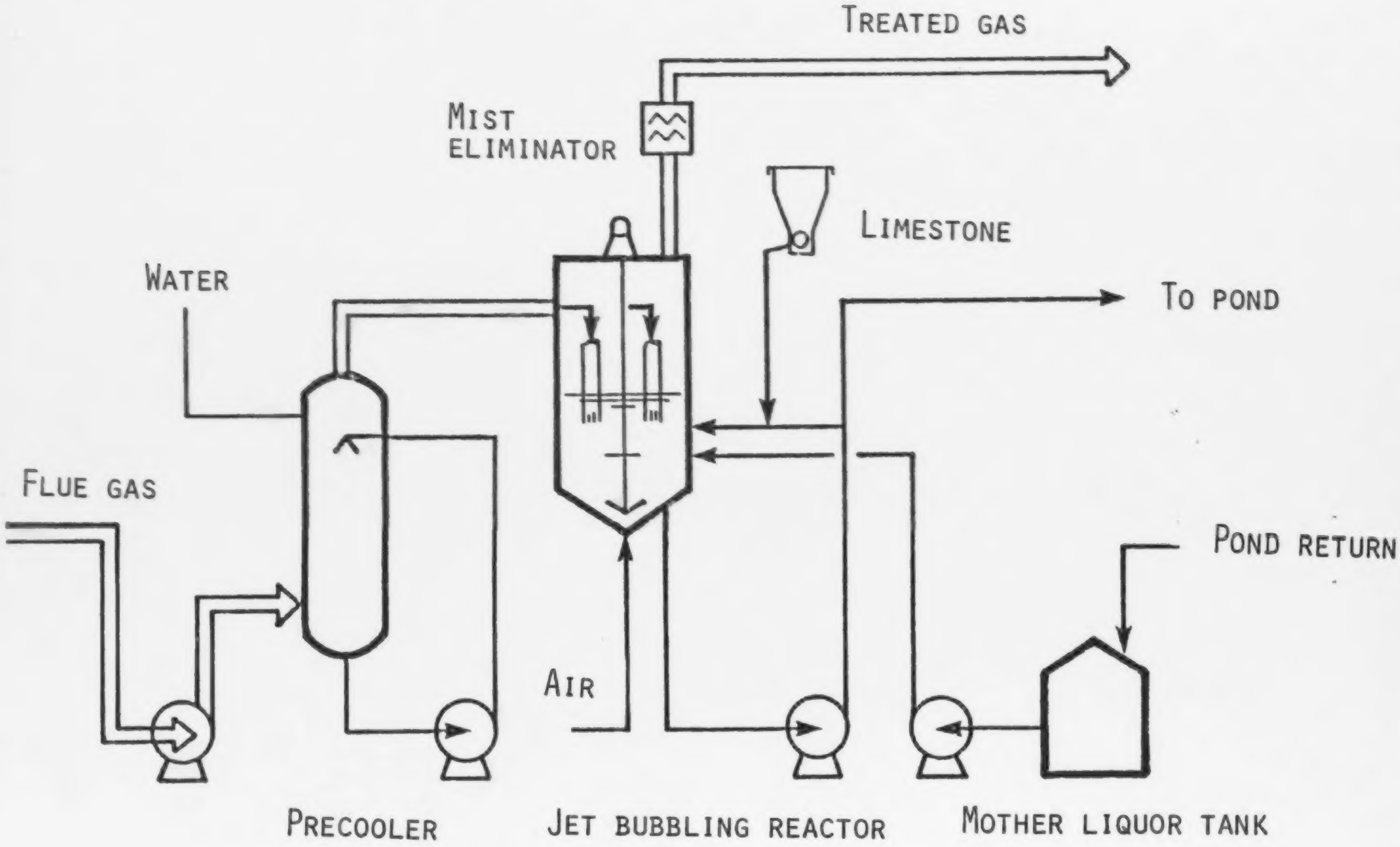

TREATED GAS
MIST ELIMINATOR
LIMESTONE
WATER
TO POND
FLUE GAS
POND RETURN
AIR
PRECOOLER
JET BUBBLING REACTOR
MOTHER LIQUOR TANK

Figure 28. Simplified flow diagram for Chiyoda Thoroughbred 121 process.

One potential problem with the CT-121 is its limited ability to handle a variable load. As the gas velocity through the sparger decreases, the pressure drop decreases producing larger bubbles. This reduces the area available for mass transfer and lowers the SO_2 removal.

A second area of concern is the gypsum by-product. The presence of organics and trace elements could result in an inferior product which may not be marketable. The gypsum will then be disposed of in a landfill. Thus, land availability could limit the use of this process in some cases.

The Chiyoda Thoroughbred 121 process has been demonstrated on a 23 MW boiler at Gulf Power's Scholz Station (3,18). An existing CT-101 system was modified to the CT-121 for this demonstration.

4.1.6.4 Citrate Buffered Absorption Process--

The Citrate Absorption Process uses a buffered aqueous solution to remove SO_2 from flue gases. Sulfur is produced as a by-product by reacting the absorbed SO_2 with H_2S gas.

A simplified flow diagram for the Citrate Process is shown in Figure 29. After prescrubbing, the flue gas is contacted with a buffered aqueous solution in an impingement tray or packed bed absorber for SO_2 removal. The citrate acts as a buffer maintaining a pH of 3.5 to 4.5 throughout the system. The primary reactions which occur in the absorber are:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \qquad (59)$$

$$H\,Cit^= + H^+ \rightarrow H_2Cit^- \qquad (60)$$

Absorber liquor is contacted with H_2S in a series of reactors to form elemental sulfur by the following overall reaction.

$$HSO_3^- + H^+ + 2H_2S \rightarrow 3S + 3H_2O \qquad (61)$$

The sulfur is then concentrated and separated from the regenerated liquor. H_2S for the regeneration step can be produced by reacting reducing gas with two-thirds of the product sulfur from the process. However, this increases the cost of regeneration and the advantage of an external H_2S source (e.g., refineries, gasification plants) is readily apparent. Another problem may result from trace contaminants in the elemental sulfur from the regenerator. Trace elements carried over in the sulfur by-product could poison the catalyst. Their presence could also decrease the sulfur marketability. Another potential problem which should be considered is the control of the H_2S flow to the regeneration reactors. A specific amount must be provided for regeneration purposes. Excess H_2S must be burned in process equipment or flared.

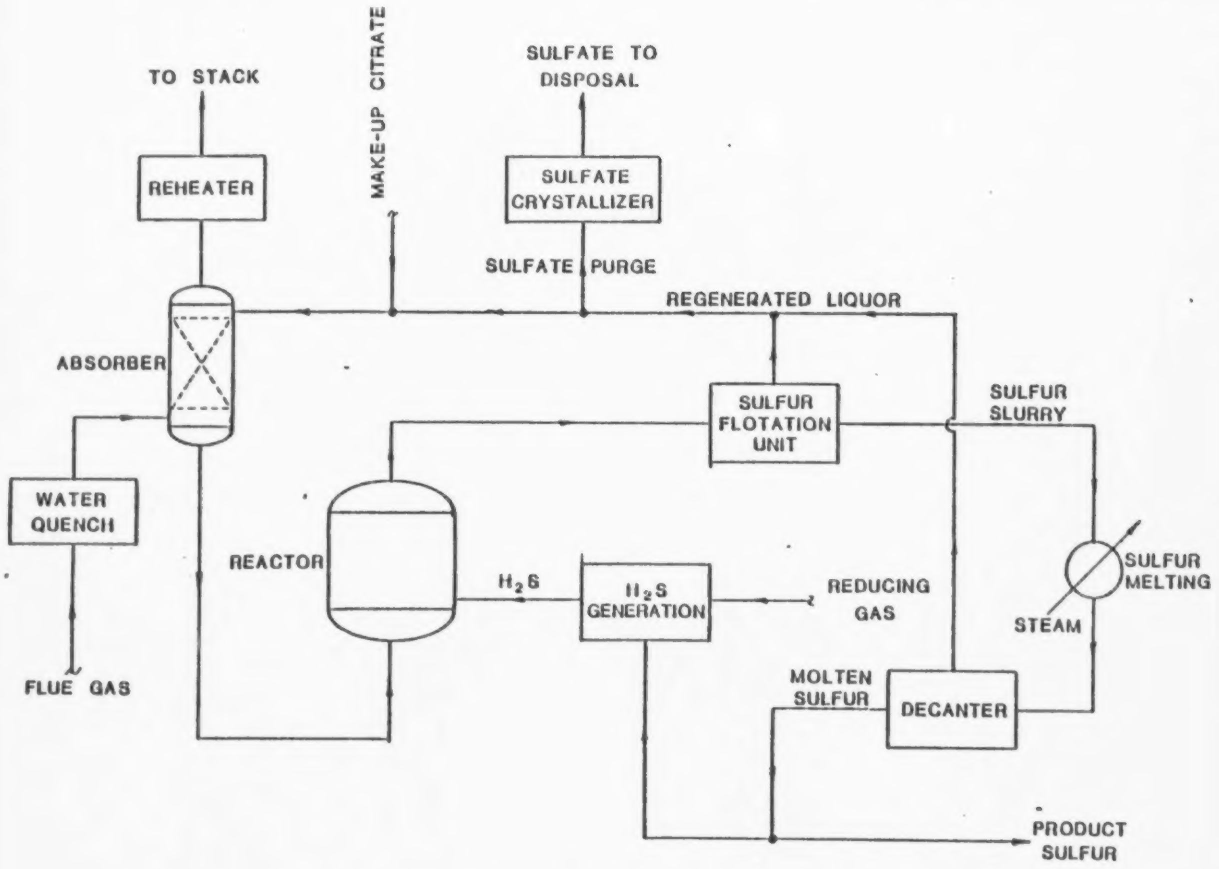

TO STACK
MAKE-UP CITRATE
SULFATE TO DISPOSAL
REHEATER
SULFATE CRYSTALLIZER
SULFATE PURGE
REGENERATED LIQUOR
ABSORBER
SULFUR FLOTATION UNIT
SULFUR SLURRY
WATER QUENCH
REACTOR
H_2S
H_2S GENERATION
REDUCING GAS
SULFUR MELTING
STEAM
FLUE GAS
MOLTEN SULFUR
DECANTER
PRODUCT SULFUR

Figure 29. Simplified flow diagram for citrate process.

The citrate process is relatively complicated compared to some other FGD processes. With the added equipment for regeneration, the citrate process will have higher capital costs than the throwaway processes. Furthermore, the H_2S production area uses technology still under development. At present, the citrate process seems most applicable to plants with an H_2S stream readily available (18). Testing of 60 MW demonstration of the citrate process was begun in the early spring of 1979 at St. Joe Mineral's coal-fired power plant in Monaca, Pennsylvania.

4.1.6.5 Sodium Throwaway Process--

Sodium Throwaway processes use either a dry sodium alkali or a wet scrubbing solution to remove SO_2 from flue gas. The wet process uses NaOH, Na_2CO_3, $NaHCO_3$ or some other sodium alkali in a wet scrubber or spray dryer for gas cleaning. The operation of the wet scrubber and spray dryer are characterized by a low L/G and a clear scrubbing liquor because of the high solubility of sodium salts.

The absorption reactions which take place in the scrubber are as follows:

$$2NaOH(l) + SO_2\ (g) \rightarrow Na_2SO_3(l) + H_2O(l) \qquad (62)$$

$$Na_2CO_3(l) + SO_2(g) \rightarrow Na_2SO_3(l) + CO_2(g) \qquad (63)$$

$$2NaHCO_3(l) + SO_2(g) \rightarrow Na_2SO_3(l) + H_2O(l) + 2CO_2(g) \qquad (64)$$

In a wet scrubbing system the majority of the scrubbing liquor is recycled back to the scrubber with a small bleed stream taken off to remove Na_2SO_3/Na_2SO_4 salts. Makeup sodium alkali is added to the bleed stream in a hold tank to precipitate the Na_2SO_3/Na_2SO_4 salts. The sludge waste is dewatered and sold or disposed of in an environmentally acceptable manner. High SO_2 concentration in the smelter/roaster gas presents no apparent removal problems with the exception of solid waste disposal.

The dry process has most often used nacholite ($NaHCO_3$) or trona ($NaHCO_3$ and Na_2CO_3) to remove SO_2 because they are cheap sources of sodium alkali. The alkali is contacted with the flue gas in one of the following ways:

- Powder reagent precoating of fabric filter bags with additional feeding of reagent into the flue gas entering the baghouse.
- Passing the flue gas through a fixed bed or fluid bed of the reagent.
- Hot zone injection with downstream removal.

Precoating of filter bags can achieve only 60 to 70 percent SO_2 removal with an alkali utilization of 50 to 60 percent. Both the countercurrent moving bed and hot zone injection methods appear capable of higher removals (90-95 percent), however, with an alkali utilization of 90 percent.

The wet scrubbing system is considered commercialized technology. The dry systems have been industrially demonstrated in different applications but are not considered commercialized technology for SO_2 control. Disposal of Na_2SO_3/Na_2SO_4 sludge in an environmentally acceptable manner is also not considered commercialized technology. This is a major problem with both the wet and dry systems.

Another limitation to the process is that it should be located near a large source of Na_2CO_3, trona, or nahcolite for economic reasons. All of these sodium minerals are located in the western part of the United States. Therefore, shipping these raw materials to a location in the eastern U.S. will be expensive (18).

4.1.6.6 Dowa Aluminum Sulfate Process--

The Dowa aluminum sulfate process consists of four major processing areas: absorption, oxidation, neutralization and filtration. Boiler flue gas is sent to a gas cooler, and then to a packed tower where SO_2 is absorbed by an aqueous solution of basic aluminum sulfate $[Al_2(SO_4)_3 \cdot Al_2O_3]$ according to reaction (65).

$$Al_2(SO_4)_3 \cdot Al_2O_3 + 3SO_2 \rightarrow Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 \qquad (65)$$

The SO_2-rich liquor is then sent to an oxidizing tower where the sulfite is oxidized to sulfate (reaction 66).

$$Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/2O_2 \rightarrow 2Al_2(SO_4)_3 \qquad (66)$$

Air is injected through specially designed nozzles, developing very fine air bubbles that accelerate the oxidation reaction. The major part of the oxidized solution is recycled to the absorber, but a fraction is neutralized with limestone in order to regenerate the basic aluminum sulfate and produce gypsum (reaction 67).

$$2Al_2(SO_4)_3 + 3CaCO_3 + 6H_2O \rightarrow$$

$$Al_2(SO_4)_3 \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 3CO_2 \qquad (67)$$

The gypsum is separated from the liquor in a thickener and centrifuged. The thickener overflow, filtrate and wash water is recycled to the absorber. A simplified flow diagram for the process is presented in Figure 30.

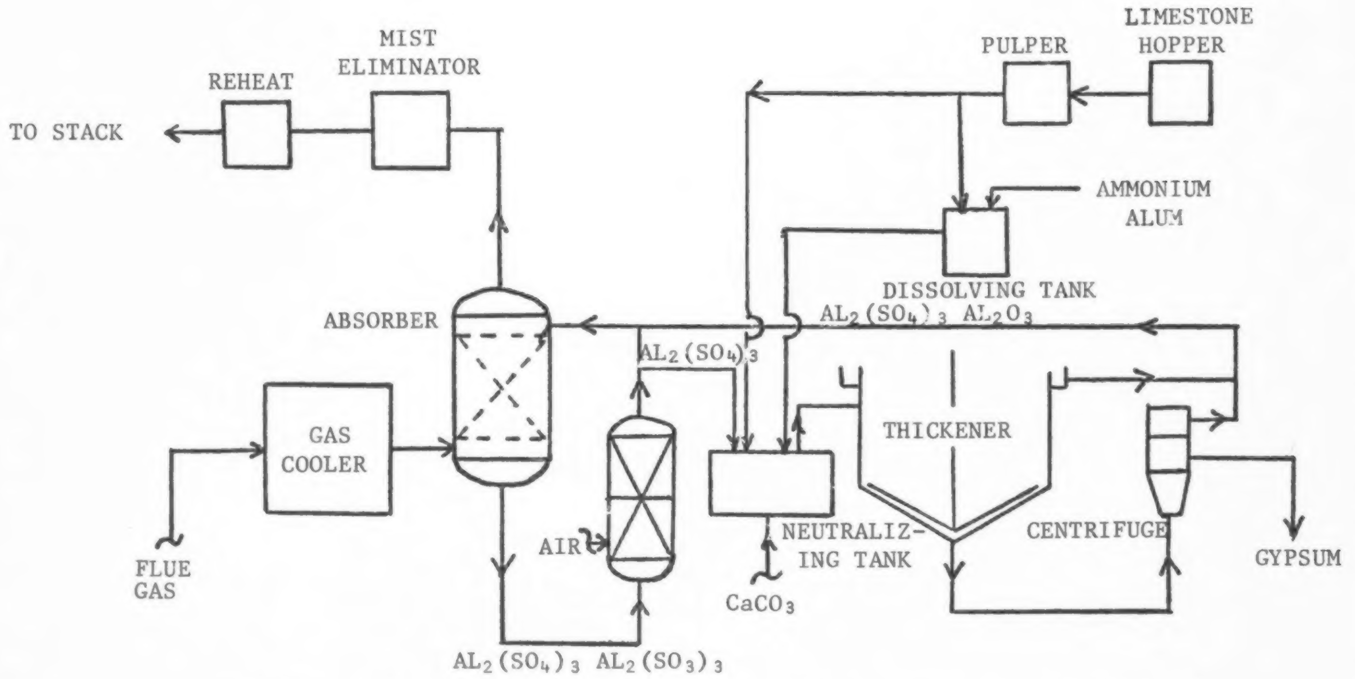

LIMESTONE HOPPER
PULPER
MIST ELIMINATOR
REHEAT
TO STACK
AMMONIUM ALUM
DISSOLVING TANK
$AL_2(SO_4)_3$ AL_2O_3
ABSORBER
$AL_2(SO_4)_3$
GAS COOLER
THICKENER
AIR
NEUTRALIZ-ING TANK
CENTRIFUGE
GYPSUM
FLUE GAS
$CaCO_3$
$AL_2(SO_4)_3$ $AL_2(SO_3)_3$

Figure 30. Simplified Flow Diagram for Dowa aluminum sulfate process

The Dowa Process seems to be well suited to smelter gas applications. It can operate at any level of oxidation and requires no sulfate purge or complex operation for sulfate removal. A unit treating 2065 scfm of waste gas from molybdenum sulfide calcination (7,500 ppm SO_2) was put into operation at Taenaka Mining Co. in October 1972. Using a TCA scrubber at an L/G of 5.0 ℓ/m^3 (37.4 gal/macf), 95 percent SO_2 removal has been attained.

The Dowa Process uses aluminum as a buffer with a resulting pH of about 4. Other buffers can be used with the same Dowa flowsheet. Buffers which will allow operation at higher pH values can potentially lower the L/G requirement. Operation at the higher pH and lower L/G also allows for simpler scrubber design. However, higher pH values (greater than 5) may require lime instead of limestone for neutralization.

The major drawback of the Dowa Process is the production of a gypsum waste product. Unless a market can be found, this must be disposed of in a landfill and land requirements can become a limiting factor. The gypsum produced from smelter gases may also contain some trace metals or organics. This could render it unsalable and may further add to disposal problems. Overall though, this process appears to be a viable alternative for smelter/roaster applications (18).

4.1.6.7 Sorption/Steam Stripping Process--

A number of process alternatives exist for a sorption/steam stripping FGD system. These alternatives differ primarily in the sorbent used. Several process options and their respective absorbents are listed below:

- NIIOGAZ Ammonia/Steam Stripping - Ammonia
- ICI Steam Stripping/Base - Aluminum Sulfate/Aluminum Choride Solution
- Peabody - Sodium Citrate
- Flakt/Boliden - Sodium Citrate
- Ethylenediamine System - Ethylenediamine
- Spring/Nobel Hoechst - Glyoxylic Acid

In addition to these absorption processes, Rohm & Haas has proposed an adsorption process based on the use of a resin absorbent.

A generalized configuration for the sorption/steam stripping process is shown in Figure 31. Flue gas is prescrubbed with water to remove HCl, and residual fly ash. SO_2 is removed by absorption in an aqueous solution in a countercurrent absorber. The feed solution to the scrubber usually corresponds to an L/G of less than 10 gal/MCF, and frequently recirculation loops are required to maintain adequate liquid loading on the packing or trays. The scrubber feed and SO_2- rich solutions are cross-exchanged for optimum heat recovery. Intermediate storage of the rich and lean solutions permits decoupling of scrubber operation from solution regeneration. The SO_2-rich solution is

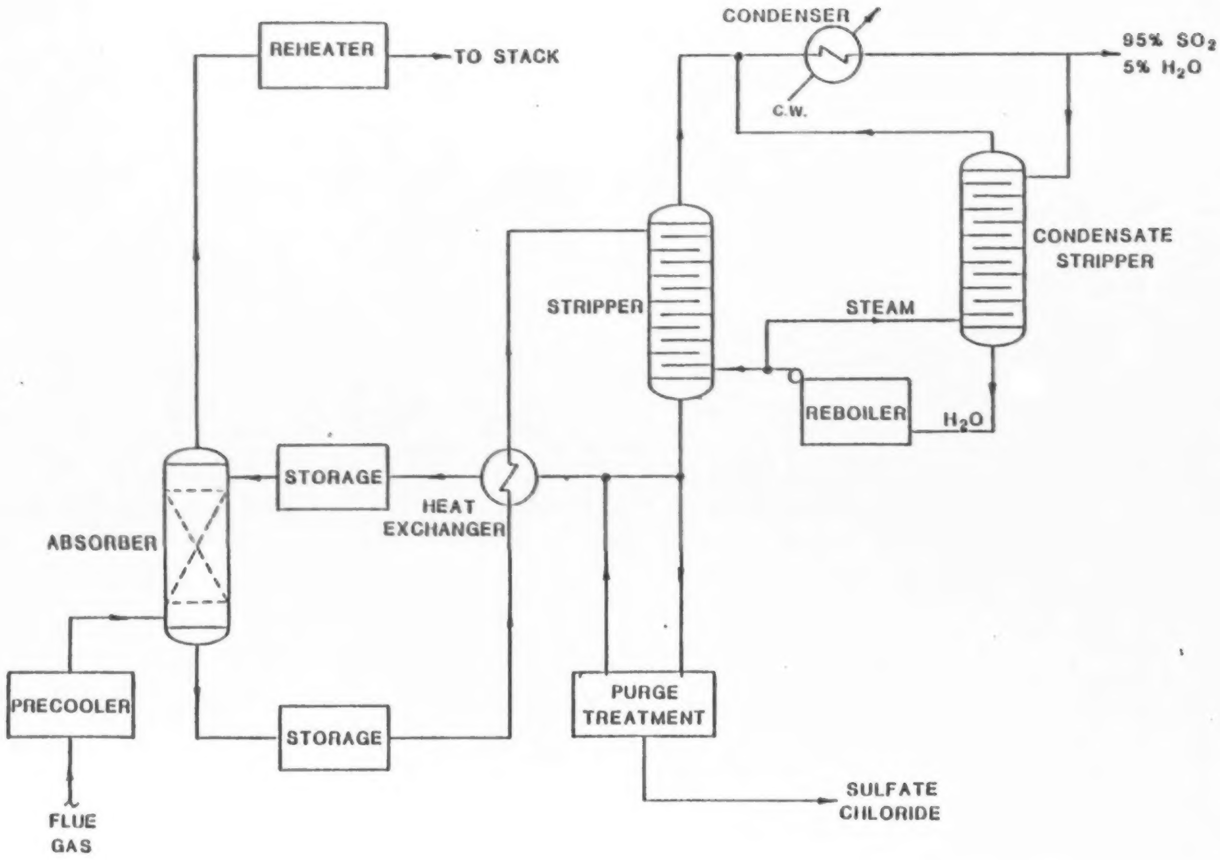

REHEATER
TO STACK
CONDENSER
C.W.
95% SO_2
5% H_2O
CONDENSATE STRIPPER
STEAM
STRIPPER
REBOILER
H_2O
ABSORBER
STORAGE
HEAT EXCHANGER
STORAGE
PRECOOLER
FLUE GAS
PURGE TREATMENT
SULFATE CHLORIDE

Figure 31. Simplified flow diagram for absorption/steam stripping process.

stripped with steam in a countercurrent condensate stripper and vaporized to produce steam for the main stripper. Normally the SO_2 product will be a gas containing about 95 percent SO_2 and 5 percent H_2O. If stripping is performed at a pressure greater than 4 atmospheres, liquid SO_2 (containing some H_2O) can be directly produced. This may be the best alternative for application such as Molycorp where the SO_2 production rate is probably too small to justify a sulfuric acid or sulfur plant. Liquid SO_2 does present special storage problems and also requires an available market. This could be a major limitation for this process in some cases.

The SO_2 product is also suitable for conversion to sulfuric acid or elemental sulfur. Trace elements in smelter application could pose a problem, however, and may result in an inferior product. Trace elements may also catalyze the oxidation of sulfite to sulfate. All of these systems require disposal of a sulfate waste product.

Most of the steam stripping alternatives should be capable of excellent SO_2 removal. However, higher removal efficiencies are probably more difficult to achieve in an ammonium sulfite/bisulfite system where complete solution stripping is not possible. Also, fume formation may be a problem with NH_3 scrubbing although lower gas temperatures (95°F) should help. Volatility and possible losses of glyoxylic acid and ethylenediamine in the scrubber are possible problems for two of the process variations.

SO_2 removal by absorption/stripping has been considered intermittently since work by H. F. Johnstone in the 1930's. Process advantages include relative simplicity and report low energy requirements. Though many of these processes have only been briefly tested, or are at the conceptual stage, their development to commercial processes could be quite rapid. Application to smelter/roaster offgases does appear feasible. However, the SO_2 product marketing may be a problem.

4.2 CONCEPTUAL DESIGN OF A LIMESTONE FGD SYSTEM FOR THE MOLYCORP MOLYBDENUM ROASTER

Application of a limestone FGD system on a concentrated SO_2, low-volume gas stream such as the one at Molycorp had not (to our knowledge) been demonstrated on a full-scale unit.* A conceptual design is presented in the following sections which incorporates data and design parameters used in many large utility applications. This information should provide a basis for a reasonable limestone system design for Molycorp. The Radian inorganic process computer simulation model is used to calculate stream flows and chemical characteristics. Finally, an economic evaluation is performed to estimate the expected capital and operating costs of a full-scale unit. A comparison of alternatives is given for different system processing areas in Appendix A. Equipment cost details are presented in Appendix B.

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*Shortly after completion of this conceptual effort, it was discovered that Duval and Union Carbide employed lime-based non-regenerable scrubbers on their molybdenum oxide production facilities at Sierrita, Arizona and Bishop, California, respectively.

The limestone FGD system has been chosen for the FGD conceptual design because it: (1) is the most widely used FGD, (2) has the most data reported in literature, and (3) is generally the most inexpensive system over the life of a plant. The limestone system costs will provide a basis for comparing costs for other systems.

4.2.1 Design Basis

The current Molycorp roasting operation can produce approximately 10 million tons of molybdenum (Mo) annually. Currently, production is only 6 million tons per year, because a variance from the State of Pennsylvania called for reduced SO_2 emissions. Operation at essentially half load has allowed a one-half reduction in emission rate. Molycorp is planning to build a new roasting system which will produce 20 million pounds of Mo per year. This new system will require removal of SO_2 from the roaster offgases.

The conceptual design presented in this report is based on the current system operating at full load (10 million pounds Mo/year). The conceptual design includes a baghouse followed by the wet scrubbing system and then a wet electrostatic precipitator (ESP). The flue gas from the roaster is cooled with dilution air before the baghouse to protect the baghouse materials. In the conceptual design, it is proposed that stack gas reheat be achieved by exchange with the flue gas out of the baghouse. The system layout is shown in Figure 32. The wet ESP may be located before or after the limestone scrubber.

The estimated composition of the flue gas to the quench/prescrubber and to the limestone slurry scrubber is given in Table 9. This data is based on measurements taken during the Radian sampling trip from June 21 through June 23, 1978. The SO_2 concentration in the flue gas varies from 6,500 to 10,000 vppm SO_2 (dry) based on the sampling program data. The SO_2 concentration is dependent on the amount of dilution air added before the baghouse. The total SO_2 flow on a lb-mole per hour basis varies directly with the MoO_3 production rate.

The oxidation of sulfite to sulfate in the liquid phase of a limestone slurry scrubbing process is a very important parameter. The concentration of sulfate ($SO_4^=$) and calcium (Ca^{++}) in the scrubbing liquors will determine the relative saturation of the $CaSO_4 \cdot 2H_2O$ solids. It has been shown from experience with utility-sized units that above a relative saturation of 1.3 to 1.4 calcium sulfate will nucleate on equipment and form scale. Scale is very undesirable in a limestone slurry process in that it plugs equipment and causes major maintenance problems. It has also been shown, however, that if 15 percent or less of the SO_2 is oxidized in the liquid phase, the sulfate will be removed from the system as a coprecipitated solid with the calcium sulfite. When the sulfate is removed as a coprecipitate, the calcium sulfate will generally be subsaturated, and then there is no scaling problem. A detailed discussion of the coprecipitation in a limestone slurry process is given in the EPA report entitled "Experimental and Theoretical Studies of Solid Solution Formation in Lime and Limestone SO_2 Scrubbers, Volume I and II" (11).

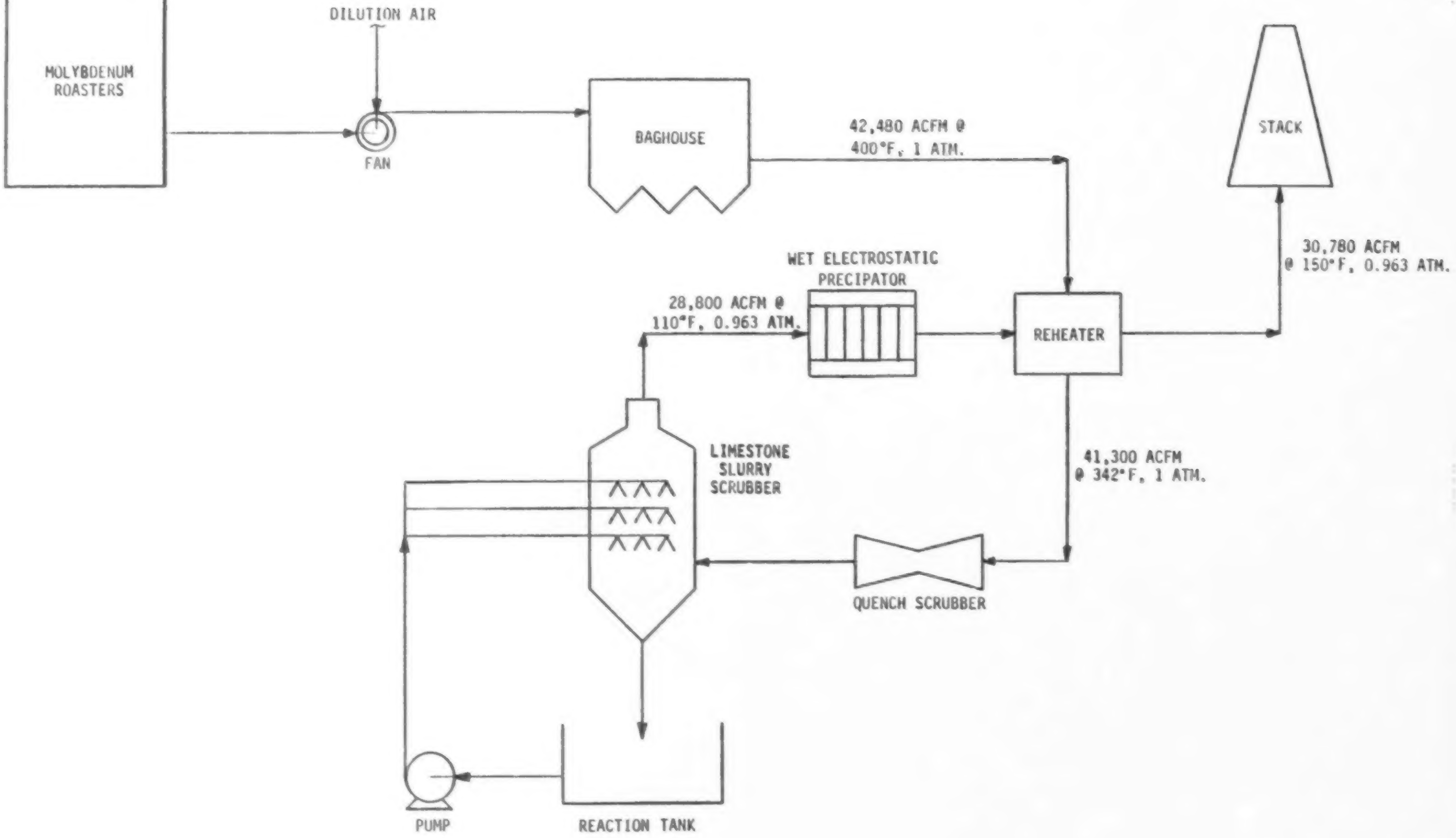
DILUTION AIR
MOLYBDENUM ROASTERS
FAN
BAGHOUSE
42,480 ACFM @ 400°F, 1 ATM.
STACK
30,780 ACFM @ 150°F, 0.963 ATM.
WET ELECTROSTATIC PRECIPATOR
28,800 ACFM @ 110°F, 0.963 ATM.
REHEATER
LIMESTONE SLURRY SCRUBBER
41,300 ACFM @ 342°F, 1 ATM.
QUENCH SCRUBBER
PUMP
REACTION TANK

Figure 32. Simplified flowscheme of the particulate and limestone FGD removal processes.

TABLE 9. ESTIMATED MOLYCORP FLUE GAS COMPOSITIONS AND FLOW

	Before Quench/ Prescrubber	Before Limestone Slurry Scrubber
Gas Flow (acfm)	41,300	28,800
Temp (°F)	340	110
Pressure (atm)	0.988	0.963
Composition (mole %)		
N_2	76.55	72.08
O_2	18.90	17.03
CO_2	1.34	1.26
SO_2	0.72	0.68
SO_3 (as H_2SO_4)	160 ppm	158 ppm
H_2O	3.25	8.92

The Molycorp limestone scrubbing system is assumed to operate at 15 percent oxidation and in a subsaturated mode. Although the oxygen concentration in the flue gas is high, the SO_2 loading on the scrubber solutions is also high. In utility experience, high SO_2 concentration in flue gases has generally resulted in lower percent oxidation than gases containing low SO_2 concentrations. The 15 percent oxidation rate is further supported by results from the bench-scale lime scrubber used at Molycorp by Radian. Electromicrophotographs of the sludge material showed a rosette-type crystal structure typical of a sulfite or sulfite/sulfate coprecipitate crystal. A sulfate sludge generally consists of larger rod-like crystals. Radian's simulation program also calculated subsaturation of calcium sulfate in scrubbing liquors from the bench-scale unit based on the chemical analysis of these liquors.

The limestone stoichiometry is a major consideration in a limestone FGD system design. The Molycorp design assumes a 1.10 stoichiometry based on SO_2 removed. At this stoichiometry it is felt that limestone consumption and scale formation potential is minimized. The limestone used in the design is assumed to contain 0.5 weight percent reactive magnesium. A greater amount of reactive magnesium in the limestone will help achieve greater SO_2 removal.

The liquid-to-gas ratio for the conceptual design is based upon the expected liquid phase alkalinity in the scrubber. The alkalinity is provided by limestone dissolution in the reaction tank and solids dissolution (such as $CaCO_3$ and $CaSO_3 \cdot \frac{1}{2}H_2O$) in the scrubber. The dissolution and precipitation are estimated from data obtained in literature and from Radian experience and testing. The solids dissolution in the scrubber is estimated at one (1) percent of the incoming calcium carbonate solids. This assumption is based on Radian pilot plant data for a high-sulfur, coal-fired boiler.

The $CaCO_3$ dissolution rate and sulfite/sulfate precipitation rate determine the size of the reaction tank for a limestone FGD system. The tank must be large enough to dissolve the $CaCO_3$ which provides alkalinity for SO_2 removal in the scrubber. It must also be large enough to precipitate the equivalent amount of sulfur species which are removed in the scrubber. In this conceptual design the sulfate is expected to leave the system as a coprecipitate with the sulfite. Therefore, solids precipitation specifically to control the relative saturation of $CaSO_4 \cdot 2H_2O$ is not a problem. The hold tank is then dependent on the $CaCO_3$ dissolution rate. Adequate dissolution can be obtained with a hold tank solids residence time of 1000 minutes.

The SO_2 scrubber used in the conceptual design is a spray tower with three spraying sections. It is assumed that the SO_2 scrubber is preceded by a venturi prescrubber which humidifies and cools the flue gas before entering the scrubber. Although a venturi prescrubber is used, a spray or packed tower can perform the same function. The design of the prescrubber can also include potential removal of trace soluble metals and acids (i.e., HCl) in the flue gas. Removal of these species in the prescrubber minimizes the dissolved solids buildup in the SO_2 scrubber.

As previously mentioned, the SO_2 scrubber is a spray tower with three spray stages. The major design concerns in the scrubber are mass transfer area and solution residence time. These design concerns become more critical with higher desired SO_2 removals. By lengthening the scrubber and adding more spray stages both the mass transfer area and slurry residence times are increased. However, a larger scrubber means added capital costs. A further discussion on different types of scrubbers is given in Appendix A.

As shown in Figure 33, the conceptual design is based on a gas/gas type reheater. This reheater would utilize the heat from the hot flue gas from the baghouse to warm the exit gas from the scrubber. A more detailed discussion of reheat alternatives is also given in Appendix A.

Sludge disposal in the conceptual design is assumed to be handled in an off-site landfill. The sludge is concentrated in a thickener/vacuum filter arrangement and then hauled by truck twenty miles to the landfill. The landfill is designed with a twenty-year plant life and has a volume of approximately 350 acre-feet. The landfill is constructed by scraping an area and building dikes in a shape of a square pond. The pond is then lined with 20 mil PVC liner and the liner is covered by one foot of clay earth cover for protection. The liner is designed to prevent leaching of soluble materials into the area water table. The bench-scale scrubber sludge was analyzed for heavy metals. It was found that the impurities in the sludge were introduced from the lime used in the scrubber. The contribution from the flue gas to the impurities was negligible. There are several alternatives to off-site landfilling which are discussed in Appendix A.

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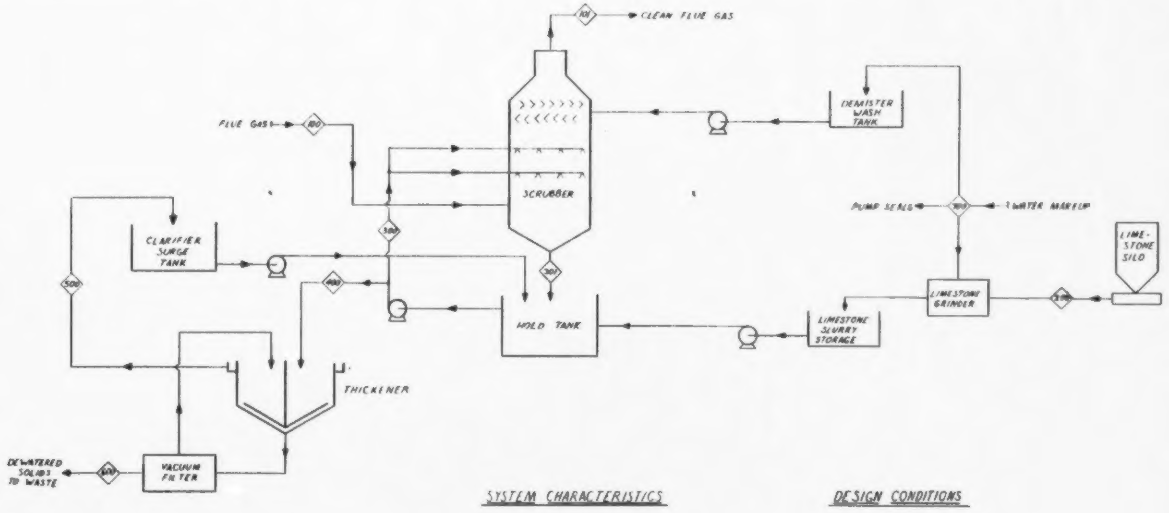

CLEAN FLUE GAS
101
FLUE GAS
100
SCRUBBER
DEMISTER WASH TANK
PUMP SEALS
700
WATER MAKEUP
LIME-STONE SILO
200
LIMESTONE GRINDER
LIMESTONE SLURRY STORAGE
HOLD TANK
301
300
400
CLARIFIER SURGE TANK
500
THICKENER
VACUUM FILTER
600
DEWATERED SOLIDS TO WASTE

STREAM NUMBER	200	300	301	400	500	600	700
TOTAL FLOW lb/hr	3000	4.61×10^6	4.61×10^6	32,850	24,500	7,731	9,075
SLURRY SOLIDS CONTENTS WT %		12.0	12.0	12.0	0.0	50	0.0
TOTAL FLOW GPM		8,540	8,540	53.8	49.0	10.8	4.5
pH		6.4	4.87	6.4	6.7	6.7	8.0
TEMPERATURE °F		110	110	110	110	110	60
LIQUID COMPOSITION (MOLALITY)							
SO_2		2.87×10^{-3}	8.34×10^{-3}	2.87×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	–
CO_2		5.84×10^{-3}	4.20×10^{-4}	5.84×10^{-3}	7.12×10^{-3}	7.12×10^{-3}	4.55×10^{-4}
SO_3		5.45×10^{-3}	5.55×10^{-3}	5.45×10^{-3}	5.48×10^{-3}	5.48×10^{-3}	6.25×10^{-4}
CaO		1.25×10^{-3}	1.35×10^{-3}	1.25×10^{-3}	1.21×10^{-3}	1.21×10^{-3}	8.74×10^{-4}
MgO		4.67×10^{-3}	4.67×10^{-3}	4.67×10^{-3}	4.67×10^{-3}	4.67×10^{-3}	3.29×10^{-4}
Na_2O		–	–	–	–	–	–
HCL		7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.49×10^{-4}	7.06×10^{-4}
TDS, WPPM				7,437	7,375	7,375	156
SOLIDS COMPOSITION WT %							
$[(CaSO_3)\cdot.86\cdot(CaSO_4)\cdot.14]\cdot\frac{1}{2}H_2O$		87.11	87.16	87.11		87.21	
$CaSO_4\cdot 2H_2O$							
$CaCO_3$	95.0	7.38	7.31	7.38		7.38	
$MgCO_3$	0.5						
INERTS	4.5	5.51	5.53	5.53		5.51	

SYSTEM CHARACTERISTICS

LIQUID-TO-GAS RATIO	300 GALLONS/ 10^3 ACF (SAT'D)
HOLD TANK VOLUME	32,000 GALLONS
THICKENER DIAMETER	39 FT.
VACUUM FILTER AREA	43.9 FT.^{2}

DESIGN CONDITIONS

FLUE GAS ANALYSIS AND FLOW

	100	101
ACFM	28,800	28,720
lb MOLES/hr.	4,000	3,992
lbs/hr.	112,900	112,300
TEMPERATURE °F	110	110
PRESSURE PSIA	14.16	14.19
COMPOSITION MOLE % COMPONENT		
SO_2	0.68	0.03
SO_3	0.03	0.03
HCL	NIL	NIL
O_2	17.03	16.99
N_2	72.08	72.11
H_2O	8.92	8.93
CO_2	1.26	1.91
TOTAL	100.00	100.00

NOTE: ALL VALUES ARE FOR TOTAL SYSTEM FLOW

Figure 33. Molycorp limestone scrubbing system.

4.2.2 Limestone FGD System Design Results

Using the design basis provided in the previous section, a total limestone system can be sized. Systems flows and chemical characteristics are estimated by the Radian aqueous inorganic computer process simulation program.

This program combines a chemical equilibrium program with a modular process sequence routine. The equilibrium program estimates equilibrium compositions of inorganic solid-liquid-gas mixtures similar to those found in limestone FGD systems. The chemical composition results are based on chemical equilibria theory and data obtained from literature and Radian experimentation. The system simulator performs material and energy balances around specific equipment items (modules) and puts the results in stream vectors which can be used to tie the entire system together.

Certain assumptions about system operation are made to use the simulation program. These assumptions include oxidation rate, removal efficiency, and percent solids dissolution in the scrubber. As mentioned before, the oxidation rate at Molycorp is estimated at 15 percent of the SO_2 removal rate. The removal efficiency is specified at 95 percent. At this removal level, Molycopy will be able to adequately meet the existing Pennsylvania State regulation of 500 ppm SO_2 maximum in any process effluent gas. Also, as previously mentioned, the percent solids dissolution is assumed to be one (1) percent of the incoming calcium carbonate solids to the scrubber.

The results of the computer simulation are shown in Table 10 and Figure 43. In Table 10, calcium sulfate is shown to be in a subsaturated mode. This indicates that sulfate scale should not be a problem provided that the 15 percent oxidation is valid. Proposed pilot plant testing should verify these results. The flows shown in Figure 43 are also used in the next section to size equipment for the conceptual design economics.

TABLE 10. RESULTS OF THE COMPUTER SIMULATION OF THE MOLYCORP LIMESTONE FGD PROCESS

Flue Gas	
Inlet SO_2 concentration	7460 ppm, dry
Outlet SO_2 concentration	375 ppm, dry
Scrubber Bottoms Stream	
pH	4.9
Partial pressure of SO_2	11.1×10^{-6}atm
Relative saturation	
$CaCO_3$	7.3×10^{-5}
$CaSO_3 \cdot \frac{1}{2}H_2O$	0.516
$CaSO_4 \cdot 2H_2O$	0.917
Scrubber Feed Stream	
pH	6.4
Partial pressure of SO_2	4.5×10^{-8} atm
Relative saturation	
$CaCO_3$	0.40
$CaSO_3 \cdot \frac{1}{2}H_2O$	2.40
$CaSO_4\ 2H_2O$	0.843

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4.2.3 Economic Evaluation

The economic evaluation used in this report is similar to previous evaluations by TVA estimating cost for utility-sized FGD systems. This type of analysis should give a reasonable first estimate of installed equipment and operating costs.

All pieces of equipment which are needed for the Molycorp FGD facility are sized based on the computer simulation results. The design parameters come from design data primarily for utility-sized operations. Good reliability should be expected when applying these parameters to the smaller Molycorp equipment.

All costs for this study have been escalated to expect mid-1979 costs. (The estimated Chemical Engineering cost indices for mid-1979 are 247 for equipment and machinery and 190 for labor.) The tables showing the detailed equipment costs are located in Appendix B of this report. Installation costs are estimated based on TVA and Radian data. Factors are applied to give costs for erection, piping, insulation, ductwork, foundations, structural support, electrical, instrumentation, buildings excavation and other miscellaneous items. The final results are shown in Table 11. The location escalation factor is applied to show the cost differential for a plant constructed in the Pittsburgh area compared to a midwest plant location.

In order to determine the total capital investment, additional costs must be applied for items such as contingency, fees, design, etc. Those added costs, shown in Table 12, are estimated as a percentage of the direct investment. Engineering design and supervision is estimated at eleven (11) percent, construction field expense at thirteen (13) percent, contractor fees at seven (7) percent, and contingency at eleven (11) percent of the direct investment. Additional costs are also shown as allowances for start-up and modifications, interest during construction and working capital. The final total capital investment is $5,750,000 (mid-1979).

Operating costs for the Molycorp FGD facility are estimated in Table 13. The costs are based on mid-1979 data with the plant operating 90 percent of the time. Included in the operating costs are manpower and fuel costs for the off-site sludge trucking operation. As shown in the table, the major operating cost is the capital charge. The capital charge rate (26.2 percent of total capital investment) is based on the following assumptions:

- Straight line depreciation of the plant over 20 years.
- 100 percent financing at nine percent interest.
- An expected 15 percent return on investment.
- A 48 percent tax rate.

TABLE 11. MOLYCORP LIMESTONE FGD SYSTEM DIRECT INVESTMENT (THOUSANDS)

Direct Costs	Raw Materials Handling	Feed Preparation	Quench/ Prescrubber	SO_2 Scrubbing	Gas Reheat Handling	Solids Disposal	Utilities Services	Construction Facilities (5%)	Totals
Equipment									
Materials	45	207	30	279	125	295	229	-	1210
Labor	16	38	12	47	21	97	10	-	241
Piping and Insulation									
Materials	-	7	3	39	-	2	5	-	56
Labor	-	19	3	45	-	2	5	-	74
Ductwork, Dampers, Chutes, supports, etd.									
Materials	6	3	-	-	133	-	-	-	142
Labor	4	4	-	-	58	-	-	-	66
Concrete Foundations									
Materials	6	4	-	3	1	1	-	-	15
Labor	44	24	2	11	7	5	-	-	93
Excavation, Site Preparations, Railroads, and Roads	-	-	-	-	-	585	20	-	605
Structural									
Materials	5	-	4	18	-	-	-	-	27
Labor	6	-	2	10	-	-	-	-	18
Electrical									
Material	17	31	2	11	17	4	10	-	92
Labor	45	62	2	16	25	10	15	-	175
Instruments									
Materials	3	26	2	18	7	1	5	-	62
Labor	2	17	1	11	3	-	2	-	36
Paint & Miscellaneous									
Materials	-	-	-	-	-	-	2	-	2
Labor	3	4	1	2	-	1	3	-	14
Buildings									
Materials	-	35	-	-	-	-	-	-	35
Labor	-	45	-	-	-	-	-	-	45
Location Escalation Factor (8%)	16	42	5	41	32	80	24	-	240
Construction Facilities	-	-	-	-	-	-	-	162	162
Subtotal Direct Investment	218	568	69	551	429	1083	330	162	3410

Values for Equipment - Materials are derived from Appendix B, Table B1-B7.

TABLE 12. MOLYCORP LIMESTONE SCRUBBER - SUMMARY OF CAPITAL INVESTMENT (Mid-1979)

	Investment ($)	Percent of Direct Investment
Raw Materials Handling	218,000	6.4
Feed Preparation	568,000	16.7
Quency/Prescrubber	69,000	2.0
SO_2 Scrubbing	551,000	16.2
Gas Reheat/Handling	429,000	12.5
Solids Disposal	1,083,000	31.7
Utilities/Invoices	330,000	9.7
Construction Facilities	162,000	4.8
Subtotal Direct Investment	3,410,000	100.0
Engineering Design and Supervision	375,000	11.0
Construction Field Expense	443,000	13.0
Contractor Fees	239,000	7.0
Contingency	375,000	11.0
Subtotal Fixed Investment	4,842,000	142.0
Allowance for Storage and Modifications	38,000	11.4
Interest During Construction (9%/annum)	43,000	12.8
Working Capital	8,000	2.5
Total Capital Investment	5,750,000	168.7

TABLE 13. MOLYCORP LIMESTONE SCRUBBER - TOTAL AVERAGE ANNUAL OPERATING COSTS (ASSUMING 90% LOAD FACTOR)

	Annual Quantity	Unit Cost,$	Total Annual Cost $	Percent of Total Annual Operating Cost
Direct Costs				
Delivered Raw Limestone	11,830 tons	7.00/ton	82,800	3.23
Subtotal			82,800	3.23
Conversion Costs				
Operating Labor and Supervision	34,160 man-hr	10.00/man-hr	341,600	13.30
Utilities				
Fuel Oil	77,970 gal.	0.50/gal.	39,000	1.52
Process Water	2.14 x 10^6 gal.	0.12/10^3gal.	300	neg
Electricity	2.60 x 10^6 kwh	0.0275/kwh	71,500	2.79
Maintenance (9% D.I.)			305,000	11.88
Analyses	2,630 man-hr	11.00/man-hr	28,900	1.13
Subtotal			786,300	30.62
Subtotal Direct Costs			869,100	33.85
Indirect Costs				
Average-Capital Charges at 26.2% of Total Capital Investment			1,507,000	58.70
Overhead				
Plant 20% Conversion Costs			157,000	6.12
Administrative, 10% Operating Labor			34,200	1.3
Subtotal Indirect Costs			1,698,200	66.15
Total Annual Operating Cost			2,567,000	100.00

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TVA calculated expected capital and operating costs for industrial size boiler limestone FGD operations. The flue gas flows from the boilers are similar to the flue gas flow from Molycorp's roasters. Table 14 compares the capital and operating costs of two different size boilers to the molybdenum roaster. From this table, it appears the Molycorp costs may be low, however, they should be a reasonable first estimate.

TABLE 14. COMPARISON OF INDUSTRIAL SIZE BOILER FGD COSTS TO THE MOLYCORP COSTS

	Molycorp	TVA (7.5 MW)[1]	TVA (15 MW)[1]
Flue gas flow rate (acfm)	28,800	24,780	49,570
Flue gas temp. from scrubber (°F)	110	133	133
Flue gas pressure (atm)	0.963	1.0	1.0
SO_2 Conc. (ppm, dry)	7,460	2,325	2,325
Percent SO_2 removal	95	90	90
Limestone stoichiometry	1.10	1.20	1.20
L/G [gallon/10^3 acfm (sat'd)]	300	94	94
Total capital investment (x 10^6\$, mid-1979)	5.72	6.27[1]	7.53[1]
Annual operating cost[2] (x 10^6\$, mid-1979)	2.56	2.00	2.45

[1] Does not include a clarifier or vacuum filter.

[2] The capital charge rate for Molycorp is 26.2% while the TVA (utility) rate is 17.2%. The difference comes from differences in plant life, tax rate, depreciation, interest rates, return on investment and debt-to-equity ratio.

4.2.4 Process Design Alternatives

Areas of the scrubbing facility such as limestone additives, quench/prescrubber, scrubber, reheat, and solids handling do offer processing alternatives. Anyone involved in the design of a limestone FGD system should be aware of the type of process alternatives which are presented in Appendix C of this report.

Other process areas concerning the limestone handling and feed preparation will not have many design alternatives. However, one possible alternative is to use a limestone storage bin instead of an open pile as proposed in the conceptual design. A bin will allow more ease in handling the limestone solids with less fugitive particulate emissions. The major drawback is the added capital cost for the silo.

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APPENDIX A - LIMESTONE FGD SYSTEM ALTERNATIVES

The following sections of this appendix describe processing alternatives with respect to limestone scrubbing systems for:

(1) Limestone Additives,

(2) Quench and Limestone Scrubber Design,

(3) Reheat Designs, and

(4) Sludge Disposal

Comments are made which are pertinent to the Molycorp limestone FGD design.

Limestone Additives

The SO_2 removal capability of any scrubbing liquor can be described in terms of liquid phase alkalinity. The available alkalinity in scrubbing liquors is related to the pH and the concentration of the soluble sodium, magnesium, calcium and chloride species. Soluble compounds influence the ionic strength and are involved in the scrubber chemistry through formation of chemical complexes.

Magnesium can be introduced through magnesium additive such as $Mg(OH)_2$ and $MgCO_3$ or through reactive magnesium carbonate in the purchased limestone. In both cases an increase of available alkalinity is achieved. The buyer should be aware that often $MgCO_3$ will associate with $CaCO_3$ to form a dolomite material. The dolomite is generally unreactive with respect to limestone slurry FGD systems and will leave the system as an inert in the sludge.

Quench and Limestone Scrubber Process Alternatives

Table A-1 lists five different scrubber types that have been successfully used on limestone slurry FGD systems. Their applications have been primarily for utility flue gases which have much lower SO_2 loadings than the molybdenum roaster offgas.

The turbulent contact absorber (TCA) is a scrubber divided into several compartments. Each compartment contains several spheroids very similar to ping-pong balls. The spheroids provide a mechanism for distributing the scrubbing slurry, and thus provide more contact area for SO_2 removal. As shown in Table A-1, the TCA does not have as good a resistance to plugging as the spray tower. With the high L/G's needed at Molycorp, there is also a very real possibility of flooding the absorbers.

The grid tower or sieve plate absorber provides several contact stages of perforated plates. A thin layer of scrubbing liquor flows over the plates

TABLE A-1. COMPARISON OF SCRUBBER TYPES FOR A LIMESTONE WET SCRUBBING SYSTEM

	Scrubber Type				
Parameter	Marble Bed	TCA*	Venturi	Grid Tower	Spray Tower
SO_2 Removal Efficiency	Good	Good	Fair	Good	Good
Particulate Removal Efficiency	Good	Good	Excellent	Good	Fair
Gas Side Pressure Drop (in H_2O)	8-12	6-12	8-20	1-7	1-3
Gas Velocity (ft/sec)	3-8	6-11	125-300	6-11	5-25
Dissolution of Solids	Good	Fair	Poor	Fair	Poor
Resistance to Solids Plugging	Fair	Good	Excellent	Fair	Excellent

*Turbulent contact absorber

as the flue gas flows up through the perforations. The relatively long slurry residences times provided by the grid tower allow solids dissolution which would be helpful with concentrated SO_2 gas streams. The high L/G's could again cause problems by flooding or plugging the scrubber.

The marble bed scrubber (generally promoted by Combustion Engineering) is essentially a combination of the TCA and grid tower. Although the marbles do not move as the spheroids in a TCA, they do provide a medium for increasing SO_2 transfer area. The supporting perforated plate for the marble bed would be nearly identical to a sieve tray in a grid tower. Here again the solids dissolution ability of the scrubber may be out weighed by the potential flooding and plugging problems.

The venturi scrubber was originally designed as a particulate removal device. It does not have as good SO_2 removal characteristics as the other SO_2 scrubber mentioned here. Poor SO_2 removal and a high gas side pressure drop make the venturi undesirable for concentrated SO_2 streams requiring high SO_2 removal.

The quench/scrubber shown in the conceptual design is used to "condition" the flue gas before it enters the spray tower. This conditioning results in a cool, wet gas which has a significantly lower percentage of the highly soluble materials (such as HCl) than before the quench. The conditioning will protect equipment from large temperature drops and corrosive materials. All of the other types of scrubbers except the venturi will probably require a quench/scrubber similar to the one in the conceptual design.

The conceptual design uses a venturi scrubber for a quench/scrubber for gas conditioning. The venturi will also remove gaseous and particulate matter escaping the baghouse. The venturi would provide some particulate removal in the event of a baghouse failure. However, the quench/scrubber presently used at the existing Molycorp facility is adequate for gas conditioning for any FGD system retrofit.

Reheat Design

Flue gas reheat is an option which may or may not be required for a "cleaned" gas stream from a wet FGD system. Reasons for reheating the flue gas may include:

- protection of downstream equipment from corrosion
- reduction of acid rainout from a stack
- reduction of plume visibility
- reduction of ground level concentration of pollutants.

However, reheat requires energy to heat the cool, wet gas from the scrubber.

Several techniques have been designed to reheat the scrubbed flue gas and reduce the impact of the potential problems mentioned above. These reheat methods include:

- Inline, in which the flue gas is heated by contacting it with a heat exchanger located in the duct work downstream of the scrubber.
- Direct combustion, in which hot combustion gases generated by firing fuel oil or natural gas are mixed with the scrubbed flue gas.
- Indirect hot air, in which heated air is mixed with the scrubbed flue gas.
- Bypass, in which a portion of the boiler flue gas is routed around the scrubber and mixed with the scrubbed flue gas.
- Exit gas recirculation, in which a portion of the heated flue gas is passed through the reheater, heated to a higher temperature and then mixed with the saturated flue gas.
- Waste heat recovery, in which exchange with hot unscrubbed flue gas is used to heat the scrubbed flue gas.

Figure A-1 shows simplified schematics of all the above mentioned reheat systems.

The conceptual design assumes a waste-heat-recovery-type reheat system. This system utilize the hot (diluted) roaster offgas to heat the wet scrubber gas approximately 40°F (from 110°F to 150°F). The hot roaster gas is cooled from 400°F to approximately 340°F. The hot, undiluted roaster offgas can also be considered as a possible source of reheat energy.

The major problem with waste heat recovery or any system which requires an inline heat exchange bundle is corrosion. A lowering of the gas temperature can cause sulfuric acid (H_2SO_4) condensation to occur. For the Molycorp system, the acid dew point is estimated at 350°F for a gas stream containing 500 ppm SO_3 and eight percent water and 315°F for 100 ppm SO_3 and eight percent water. The corrosion problem can be minimized by proper materials of construction such as Inconel 625. The indirect hot reheat and the direct combustion reheat do not have corrosion problems because they do not use inline reheat bundles.

Reheat by waste heat recovery has not been demonstrated in commercial FGD application. Metallurgical requirements may be very costly. If corrosion becomes a major problem, indirect hot reheat or direct combustion reheat are the best alternatives. Flue gas bypassing was not considered a good reheat method in that (1) for high SO_2 removal, bypassing will not provide enough heat energy and (2) bypassing of flue gas to provide sufficient reheat may not provide sufficient SO_2 removal to meet the required levels of reduction.

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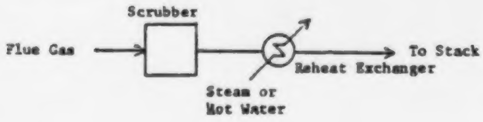
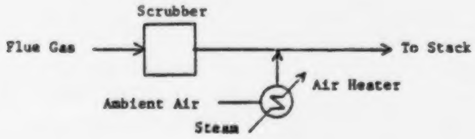
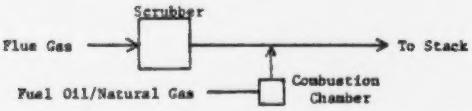

Scrubber
Flue Gas
To Stack
Reheat Exchanger
Steam or
Hot Water

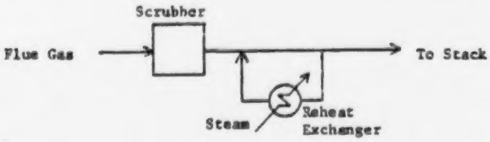
A) Inline Reheat


Scrubber
Flue Gas
To Stack
Air Heater
Ambient Air
Steam

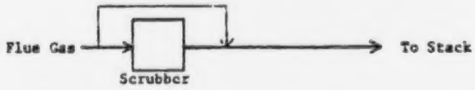
B) Indirect Hot Air Reheat


Scrubber
Flue Gas
To Stack
Fuel Oil/Natural Gas
Combustion
Chamber

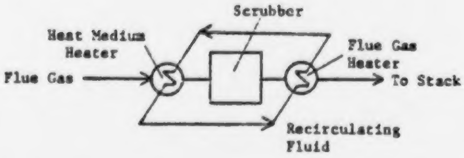
C) Direct Combustion Reheat


Scrubber
Flue Gas
To Stack
Steam
Reheat
Exchanger

D) Exit Gas Recirculation Reheat


Flue Gas
To Stack
Scrubber

E) Bypass Reheat


Scrubber
Heat Medium
Heater
Flue Gas
Flue Gas
Heater
To Stack
Recirculating
Fluid

F) Waste Heat Recovery Reheat

Figure A-1. Simplified schematics of various reheat configurations.

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Sludge Disposal Alternatives

The sludge disposal method considered in the conceptual design assumes the sludge is concentrated to 50 wt. percent solids in a thickener/vacuum filter arrangement and then trucked to a landfill 20 miles away. The landfill is approximately 30 feet deep and covers 22 acres. To prevent leaching, the landfill is lined with a 20 mil PVC liner and then covered with one foot of clay earth covering. This section will examine four alternative methods to the sludge disposal method in the conceptual design:

Alternative 1 - On-site ponding of the sludge without a thickener/ vacuum filter.

Alternative 2 - Off-site ponding and pumping the sludge 20 miles to the pond.

Alternative 3 - Chemical fixation of the sludge.

Alternative 4 - Forced oxidation of FGD sludge.

Alternative 1 - On-site Ponding--

On-site ponding is a good alternative providing there is enough room near the roaster/FGD system for a pond. The 10 million pounds Mo per year conceptual design estimated a landfill volume of 350 acre-feet for a twenty year plant life. A pond would have to be of similar size to the landfill if it can be assumed that the solids will settle to at least a 50 weight percent mixture with water. On-site ponding eliminates the large capital cost items of the thickener and vacuum filter and replaces them with pipes and pumps for sludge going to the pond and supernatent return. In areas where rainfall exceeds evaporation water will tend to accumulate in the ponds and can cause water balance problems. The pond will be constructed similar to the landfill with a PVC liner and one foot of clay earth cover.

Alternative 2 - Pump to Off-site Pond--

Although pumping sludge to an off-site pond sounds like a reasonable alternative, economic studies indicate that for anything but short distances trucking is much more cost effective. Figures A-2 and A-3 show information that was presented by TVA at the most recent Symposium on Flue Gas Desulfurization (1). They show that for a new 500 MW, coal-fired boiler (3.5 wt percent sulfur) the total capital investment is substantially less for trucking than pumping. However, annual operating revenue requirements are less for pumping up to about 2.5 miles. After that distance, trucking becomes more attractive on an annualized basis.

These numbers indicate that trucking of sludge may be more attractive economically. Trucking of sludge is, however, an inherently messy operation. Wet sludge has thixotropic properties and when spilled on the wet road can

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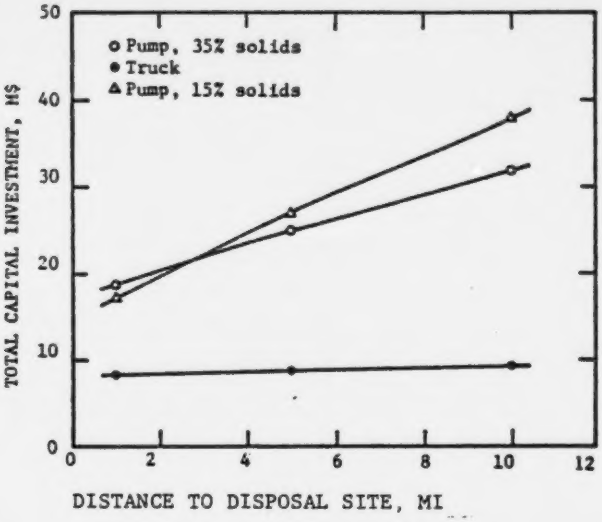

Figure A-2. Capital Cost Of Sludge Disposal. Effect Of Distance To Disposal Site And Mode Of Transport On Total Capital Investment. New 500-MW Plant.

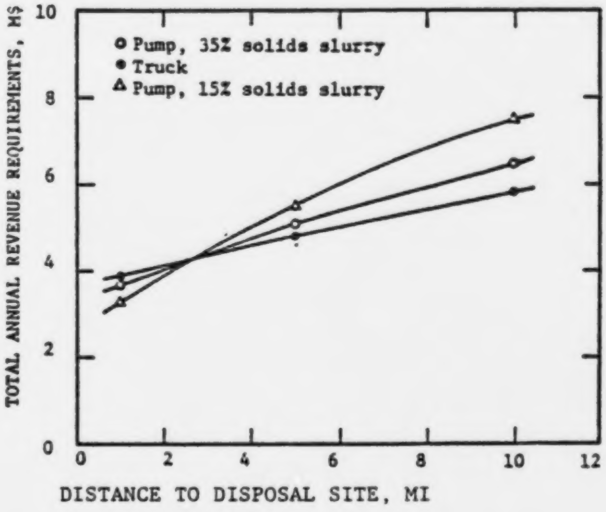

Figure A-3. Operating Costs Of Sludge Disposal. Effect Of Distance To Disposal Site And Mode Of Transport On Total Annual Revenue Requirements. New 500-MW Plant.

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be hazardous. Problems such as this may require the FGD operating company to build their own roadway for sludge hauling. This could result in a significant increase in the capital cost for trucking.

Alternative 3 - Chemical Fixation of Sludge--

Chemical fixation of limestone FGD sludges has been developed in the last few years. Chemical fixation will minimize the leaching rates and can significantly improve the mechanical properties. Both improvements are desirable if the sludge is landfilled. Three commercial chemical fixation processes are currently being promoted. These processes are: (1) the Dravo Corporation Synearth process, (2) IU Conversion Systems (IUCS) Poz-O-Tec process, and (3) Chemfix (Division of the Carborundum Company) treatment process.

In the Dravo process, the sludge is mixed with blast furnace cement and pumped to a disposal pond. The ponded material, upon settling, contains about 50 percent solids and stabilizes within 15 to 30 days through cementation reactions. The fixation can be completed in small, on-site drying ponds with the fixed sludge eventually hauled off-site by trucks to a landfill.

The IUCS Poz-O-Tec process is based on mixing the sludge with fly ash lime mixtures. The stabilization is caused by pozzolanic reactions.

The Chemfix process is a two-step inorganic chemical system which reacts with all polyvalent metal ions and sludge components. The chemical additives are sodium silicate and Portland cement. Chemfix has been applied to sludges from metal finishing, automotive assembly, sewage treatment, electronics, and FGD operations.

The cost of the chemical fixation processes is dependent on several variables such as plant life and plant size. A comparative study of these systems is presented in the proceedings to the 1978 Symposium on Flue Gas Desulfurization (2).

Alternative 4 - Forced Oxidation--

Sludge oxidation appears to be an alternative for improving sludge characteristics for sludge disposal. In an oxidized FGD system solid wastes are contacted with air to oxidize sulfite/bisulfite species to the sulfate form through the following reactions:

$$SO_3^{=}\ (\ell) + \tfrac{1}{2}O2\ (g) \rightarrow SO_4^{=}\ (\ell) \qquad \text{(A-1)}$$

$$HSO_3^{-}\ (\ell) + \tfrac{1}{2}O_2\ (g) \rightarrow SO_4^{=}\ (\ell) + H^{+}\ (\ell) \qquad \text{(A-2)}$$

when precipitated with calcium, the sulfate produces a large crystal which tends to settle faster and is more readily dewatered than the sulfite crystals.

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The forced oxidation of limestone FGD sludges in both single-loop and double-loop systems has successfully demonstrated in pilot-plant operations (10). Economically forced oxidation compares favorably against chemical fixation processes.

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Japanese FGD operations have successfully used oxidized limestone sludges in the production of gypsum wallboard. For wallboard production, particular attention must be paid to particulate size distribution, soluble salt content, and trace organic constitutents in the sludge. All these factors will affect the structural strength of the wallboard.

APPENDIX B - ESTIMATED EQUIPMENT COSTS

This appendix contains a piece-by-piece listing of all the equipment required at the Molycorp limestone slurry FGD facility. There is a capital cost given for each item. The base cost is the cost found in literature or from other Radian sources. The base cost is then escalated to expected mid-1979 costs.

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TABLE B-1. EQUIPMENT COSTS - MATERIALS HANDLING

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Unloading hopper	1	30 ft^3, carbon steel, 3 ft deep	1200 (1977)	1,400
2. Unloading hopper feeder	1	62.5 ton/hr, 2 1/2 HP motor included	2100 (1977)	2,500
3. Conveyor to storage pile	1	200 ft length, 250 ft/min 1 1/2 HP motor included	15,500 (1974	25,900
4. Solids elevator to ball mill storage bin	1	12"x7"x7 1/4" buckets 7 HP motor included	9,000 (1974)	15,000
			SUBTOTAL	44,800

TABLE B-2. EQUIPMENT COSTS - FEED PREPARATION

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Wet ball mill grinder	1	54 ton/day, 5 ft x 10 ft from 1/2" x 0 to 90 % 200 mesh includes 90 HP driver	117,000 (1978)	126,000
2. Ball mill feed bin	1	7.1 ft x 10.7 ft high carbon steel	3,600 (1974)	6,000
3. Ball mill weigh feeder	1	2.25 ton/hr, 1 1/2 HP motor included	2,700 (1974)	4,500
4. Slurry feed tank	1	13,060 gallon, carbon steel neoprene-lined	20,000 (1974)	33,400
5. Slurry feed pumps	2	30 ppm, variable speed 25' head, neoprene-lined, 1.5 HP motot	800 (1977)	1,900
6. Agitator for slurry tank	1	3 HP, neoprene coated	3,000 (1974)	5,000
7. 3-ton hoist	1	electric	12,600 (1974)	21,000
8. bag filter for crusher	1	7,000 cfm, with shaker	5,300 (1974)	8,900
			SUBTOTAL	206,000

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TABLE B-3. EQUIPMENT COSTS - QUENCH PRESCRUBBER

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Liquor recycle hold tank	1	1000 gallons, neoprene lines	5,000 (1974)	8,400
2. Agitator effluent tank	1	1 HP, stainless steel	600 (1974)	1,000
3. Recycle pumps	2	100 gpm rubber-lined 30' head, 3.0 HP motor	2,020 (1977)	4,700
4. Venturi Scrubber	1	12' high x 3.75 ' dia, neoprene-lined, 1/4" carbon steel construction	15,000 (1979)	15,000
5. Makeup water pump	2	20 gpm, 10'head, 1.0 HP motor	600 (1974)	1,000
			SUBTOTAL	30,000

TABLE B-4. EQUIPMENT COSTS - SO_2 SCRUBBING

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Spray Tower Scrubber	1	Scrubber with demister, three spray stages 8 1/4 ft dia x 37 ft high, includes turning vanes; 1/4" carbon steel, neoprene lined		47,500
2. Slurry hold tank	1	57,600 gallon, 24.5 ft dia x 16.3 ft high, neoprene lined	39,500 (1974)	66,000
3. Agitator for hold tank	1	7 1/2 HP, neoprene coated	5,400 (1974)	9,000
4. Slurry recycle pumps	4	2850 gpm each, 70 ft of head 70 HP motor included	8,500 (1974)	56,800
			SUBTOTAL	279,300

TABLE B-5. EQUIPMENT COSTS - GAS HANDLING AND REHEAT

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Hot flue gas reheater	1	560 ft^2, tube type made of inconel	29,500 (1974)	49,300 (1)
2. Ducts		75' @ 3.75' x 3,75' 350' @ 3.1' x 3.1' 1/4" carbon steel, partially rubber lined	77,400 (1977)	90,900 (2)
3. Expansion joints	6	metal bellow for ducts	2,500 (1977)	17,600 (1)
4. Dampers for bypass	3	guillotine-type. with positive pressure seal	12,000 (1977)	42,300 (2)
5. Fan	1	30,800 acfm, 12.5" H_2O ΔP, 72.5" dia wheel, 95 BHP motor included (cost is based on difference between 10" fan nd 22.5" fan)	46,000 (1976)	57,700 (1)
			SUBTOTAL	257,800

(1) Entered in Table 11 under Equipment - Materials
(2) Entered in Table 11 under Ductwork, etc - Materials

TABLE B-6. EQUIPMENT COSTS - SOLIDS DISPOSAL

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Clarifier - Thickener/ clarifier	1	39 ft dia, 10 ft deep at center, includes rake, motor and stiffening	126,700 (1977)	149,000
2. Clarifier overflow Surge tank	1	500 gallon, FRP	600 (1979)	600
3. Pump, surge tank	2	49 gpm, rubber-lined, 50' head, 1.5 HP	800 (1979)	1,600
4. Clarifier underflow pump	2	22 gpm, rubber-lined 50' head, 1.25 HP	800 (1979)	1,600
5. Vacuum filter	1	45 ft^2 rotory drum with compressor, electrical pumping and building	100,000 (1977)	132,700
6. Vacuum filtrate pump	2	10 gpm, rubber-lined 15' head, 1.0 HP	700 (1979)	1,400
7. Filtrate solids conveyor	1	10 ft 250 ft/min, 12" wide	2,700 (1977)	3,200
	1	20 ft, 250 ft/min, 12" wide	4,300 (1977	4,900
			SUBTOTAL	295,000

TABLE B-7. EQUIPMENT COSTS UTILITIES AND SERVICES

ITEM	NO.	DESCRIPTION	BASE COST (YEAR)	TOTAL MID 1979 COST
1. Dump Truck	2	12 cubic yard, diesel	35,000 (mid-1977)	82,200
2. Bulldozer	1	For sludge leveling	75,000 (mid-1977)	88,100
3. Operation building		Includes control room laboratory, and electrical storage and all accessories	35,000 (mid-1974)	58,500
4. Stores-equipment		Office equipment, shelving etc.	5,000 (mid-1974)	8,400
			SUBTOTAL	228,800

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